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Spectrophotometric and conductometric study of the complexation of *N*-salicylidene-2-aminophenol with Cu^{2+} in methanol + 1,4-dioxane binary solutions

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Abstract: The complexation reaction between *N*-salicylidene-2-aminophenol, abbreviated as SAP, with the Cu^{2+} was studied in binary mixtures of methanol and 1,4-dioxane using conductometric and spectrophotometric methods at different temperatures. The stability constants (K_f) for the 1:1 complex, Cu^{2+}–SAP, were calculated from computer fitting of the absorbance and molar conductance data against various mole ratios (c_M:c_L or c_L:c_M) in different binary solvent mixtures. A non-linear behaviour was observed for the variation of log K_f for the complex against the solvent composition. Various thermodynamic parameters (ΔH, ΔS and ΔG) for the formation of the Cu^{2+}–SAP complex were determined from the temperature dependence of the stability constants (K_f). The overall results showed that the complexation reaction is entropy driven and is affected by the nature and composition of the mixed solvents.

Keywords: *N*-salicylidene-2-aminophenol; Cu^{2+}; stability constants; binary mixtures; methanol; 1,4-dioxane.

INTRODUCTION

The coordination chemistry of nitrogen–oxygen donor ligands is an interesting area of research. A great deal of attention in this area has been focused on the complexes formed by transition metal ions with Schiff bases because of the presence of both nitrogen and oxygen donor atoms in the backbones of these ligands.[1,2] Schiff base ligands can also accommodate different metal centres in various coordination modes, thereby allowing the successful synthesis of homo and hetero metallic complexes with different stereochemistries.[3] Schiff base complexes have undergone a phenomenal growth during the recent years because of the versatility offered by these complexes in the fields of industries, catalysis, biological systems, *etc*.[4–8] Metal complexes of Schiff bases derived from sali-

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cylaldehyde and various amines have been widely investigated.[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, and elastin cross-linking.[14] Cu(II) complexes show distorted octahedral and tetrahedral symmetries due to their d^9 configuration (Jahn–Teller effect). The distortion is usually seen as an axial elongation consistent with the lability and geometric flexibility of the complex. Therefore, Cu(II) complexes may have square planar or square pyramidal geometries with weakly associated ligands in the axial position, but some Cu(II) complexes possess trigonal bipyramidal geometry. The Schiff base *N*-salicylidene-2-aminophenol (SAP) behaves as a tridentate ligand with ONO donor sites. In the complexes Cu^{2+}–SAP, three of the four coordination sites of metal ion remain occupied by nitrogen atom of the azomethine group, two oxygen atoms of the hydroxyl ions and the fourth site was reported to be occupied by a solvent or water molecule.[15] The complexes of copper with Schiff bases have wide applications in the food and dye industries, analytical chemistry, catalysis, have fungicidal, agrochemical, anti-inflammatory antiradical and biological activities.[16] The fundamental role of copper and the recognition of its complexes as important bioactive compounds *in vitro* and *in vivo* aroused an ever-increasing interest in these compounds as potential therapeutic drugs for various diseases. Hence studies on the thermodynamics of complex formation of Cu^{2+} with different Schiff bases in different solvent media are worthy of thorough studies and are demanded.[17–20]

Among the various organic solvents, methanol (MeOH) is one of the simplest amphiphile-like molecules.[21] Alcohols in non-polar solvents associate by means of hydrogen bonds into series of *n*-mers. In solvents such as 1,4-dioxane (DO) that can form hydrogen bonds with MeOH, the self-association of alcohols may be reduced or perturbed in favour of hydrogen-bonded structures when mixed together, leading to intermolecular association between MeOH and DO molecules.[22] A literature survey revealed that no reports on the thermodynamics of complex formation between the ligand SAP and transition metal ions in binary solvent mixtures exist. Hence, in this study, the complexation behaviour of SAP with Cu^{2+} in different MeOH–DO mixed solvents was investigated in order to understand the thermodynamics of complex formation between SAP and Cu^{2+} in the mixed solvents studied.

EXPERIMENTAL

Materials

Analytical grade of 2-aminophenol (s), salicyaldehyde (l), copper(II) nitrate trihydrate, $Cu(NO_3)_2 \cdot 3H_2O$ (s) were procured from Thomas Backer, India and used as received. Spectroscopic grade methanol (MeOH) and 1,4-dioxane (DO) (both of purity > 99 %, S. D. Fine Chemicals, India) were used without further purification. The Schiff base ligand *N*-salicylidene-2-aminophenol (SAP) was prepared according to a literature procedure and its purity was checked by spectroscopic and other analytical methods.[23] The various binary solvent mixtures were prepared by mass and necessary adjustments were realised 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. Utmost care was taken during the mixing process to avoid evaporation losses and moisture uptake. The mass measurements were achieved on a digital electronic analytical balance (Mettler, AG 285, Switzerland) with a precision of ±0.01 mg. The relative error in the solvent composition was about 1 %. The physical properties of these solvent–solvent mixtures are available in the literature.[24]

Preparation of the ligand

To a magnetically stirred methanolic solution of 2-aminophenol (10 mmol) in a round bottom flask was added drop wise salicylaldehyde (10 mmol). The reaction mixture was then refluxed for 2 h. After cooling, the orange red Schiff base was collected by filtration and purified by repeated recrystallisation from MeOH. The purified ligand was dried in a desiccator over anhydrous $CaCl_2$ under vacuum for several days. The orange crystalline compound was obtained in a yield of 85–90 %.

The melting point of the ligand was determined by the open capillary method. Elemental micro-analyses were realised with the aid of a Perkin–Elmer (Model 240C) analyser. The FT-IR spectrum of the ligand SAP in the range (400–4000) cm^{-1} was recorded on a Perkin–Elmer FT-IR spectrophotometer (RX-1). The ^1H-NMR spectrum was taken with a Spectrospin-Brucker AC 300 MHz spectrometer using DMSO-d_6 as the solvent and TMS as an internal reference. The mass spectra was recorded at 70 eV on a GC-MS-QP 100 Ex 5988 mass spectrometer

N-*Salicylidene-2-aminophenol (SAP)*. Yield: 85–90 %; orange crystalline compound; m.p.: 187–188 °C; Anal. Calcd. for $C_{13}H_{11}NO_2$: C, 73.22; H, 5.20; N, 6.45 %. Found: C, 73.01; H, 5.18; N, 6.45 %; FTIR (KBr, cm^{-1}): 3429.86 (3430[15]), 1630.95 (1631[15]), 1412.84 (1413[15]), 1273.92 (1274[15]); ^1H-NMR (300 MHz, DMSO-d_6, δ / ppm): 13.74 (2H, *s*, OH), 8.95 (1H, *s*, CH=N), 6.84–7.62 (8H, *m*, ArH); MS (*m/z* (relative abundance %)): 214 (100), 215 (16).

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

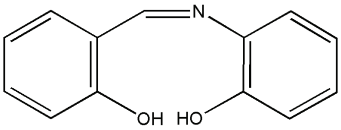

Fig. 1. Structure of *N*-salicylidene-2-aminophenol (SAP).

UV/Vis spectrophotometric titration

The absorbance spectra were recorded using a Jasco V-530 spectrophotometer equipped with a thermostated bath. During the complexation studies, the temperature of the quartz cell was maintained at 298.15±0.1 K. In the spectrophotometric titration, the addition 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}) was realised 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. The addition of metal ion solution was continued until the desired metal to ligand mole ratio (c_M:c_L) of 3:1 was achieved.

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. The measurements were made in a water bath maintained at ±0.01 K of the desired temperatures. The cell was calibrated with a standard KCl solution as described earlier.[27] and the cell constant was 1.18 cm^{-1}. During 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 using a pre-calibrated micropipette (50 µL) and the conductance of the solution was measured after each addition. The 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 AND DISCUSSION

UV/Vis spectrophotometric titration

The UV/Vis spectra of the ligand SAP and its Cu^{2+} complex in pure MeOH and in the binary mixtures of MeOH with DO are shown in Fig. 2. This figure shows that the absorption spectrum of the solution of the ligand (initially 5.0×10^{-5} mol dm^{-3}) suffered from marked changes when a solution of Cu^{2+} cations (1.3×10^{-3} mol dm^{-3}) was added in a stepwise fashion to the ligand solution until

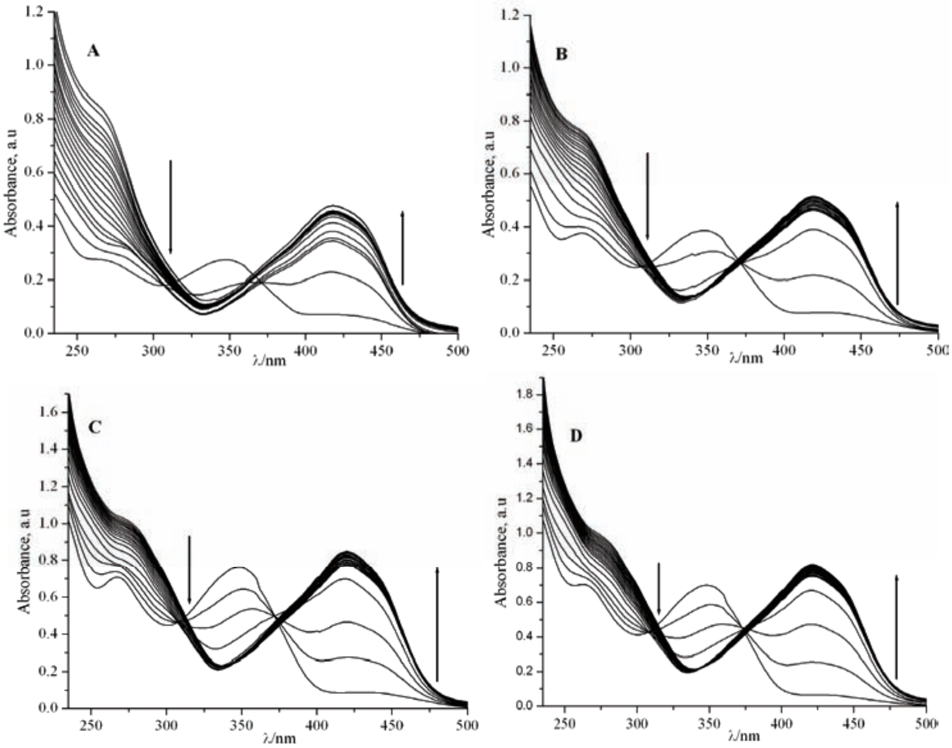

Fig. 2. UV/Vis spectra of the ligand SAP (5.0×10^{-5} mol dm^{-3}) in the presence of increasing concentration of Cu^{2+} in different solvent mixtures of MeOH and DO at 298.15 K. MeOH mass fractions (w_1) A, w_1 = 1.00; B, w_1 = 0.80; C, w_1 = 0.60; D, w_1 = 0.40.

the mole ratio (c_M:c_L) = 3:1 was achieved. Thereafter, further addition of metal solution affected no noticeable changes in the spectra. The UV/Vis spectra of the ligand showed two characteristic bands at around 270 and 348 nm. These bands originated from the azomethine chromophore and the phenol moiety, respectively. During spectrophometric titration, complex formation was indicated by a decrease in the intensity of 348 nm peak and a concomitant development of a peak at around 418 nm. The complex formation was further manifested by a strong spectral shift of about 70 nm towards longer wavelength, in comparison to the free ligand. These changes in UV/Vis spectra were due to the coordination of Cu^{2+} through the imine nitrogen atom with an additive effect from the deprotonation of phenolate groups upon chelation, thereby resulting in the formation of six and five-membered ring systems between the metal atom and ligand in the complex.[17] Thus, analysis of the spectrophotometric data was performed with absorbance values at λ = 418 nm, as shown in Fig. 3. It was evident from Fig. 3 that when the ligand SAP reacted with Cu^{2+} in MeOH and its binary mixtures with DO, it formed a 1:1 complex. The mass balance for metal–ligand (ML) complex can be given by the following relation:[25]

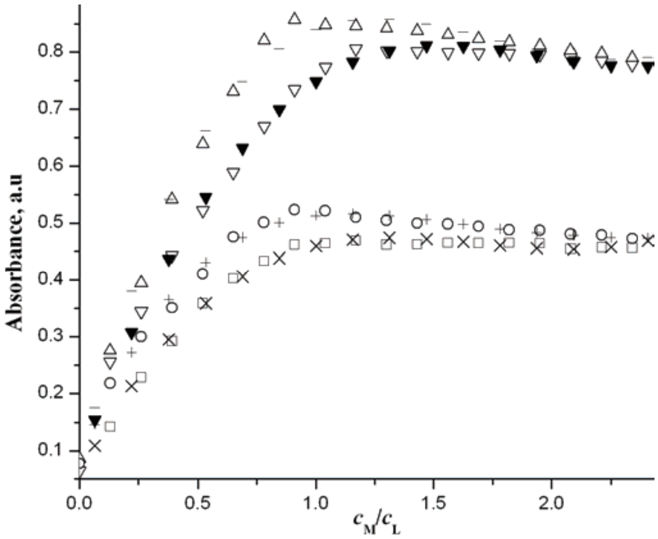

Fig. 3. Mole ratio plot (c_M:c_L) for the complexation reaction of the ligand SAP with Cu^{2+} against different mass fractions (w_1) of MeOH in the solvent mixtures at 298.15 K. Symbols for the experimental data: □, w_1 = 1.00; ○, w_1 = 0.80; Δ, w_1 = 0.60; ∇, w_1 = 0.40. Symbols for the calculated data (program generated): ×, w_1 = 1.00; +, w_1 = 0.80; -, w_1 = 0.60; ▼, w_1 = 0.40.

$$M + L \leftrightarrow ML \tag{1}$$

Therefore, the formation constant (K_f) is given by:

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

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

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

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

When [M] and [L] obtained from Eqs. (3) and (4), respectively, are substituted into Eq. (2), K_{f} is obtained as:

$$K_{\mathrm{f}} = \frac{[\mathrm{ML}]}{(c_{\mathrm{M}} - [\mathrm{ML}])(c_{\mathrm{L}} - [\mathrm{ML}])} \tag{5}$$

If only the complex absorbs at a particular wavelength, total absorbance (A) is given by:

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

or

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

where ε is molar absorptivity coefficient of the complex and at the path length l =1 cm.

When $c_{\mathrm{M}} >> [\mathrm{ML}]$, Eq. (5) could be rearranged as:

$$K_{\mathrm{f}} = \frac{[\mathrm{ML}]}{c_{\mathrm{M}}(c_{\mathrm{L}} - [\mathrm{ML}])} = \frac{A/\varepsilon}{c_{\mathrm{M}}(c_{\mathrm{L}} - A/\varepsilon)} \tag{8}$$

Rearranging the above relation, one obtains:[26]

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

Thus a linear regression of $c_{\mathrm{M}}c_{\mathrm{L}}/A$ against c_{M} gives the molar absorptivity (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 ($A_{\mathrm{cal},i}$) of each solutions were iteratively calculated and then the final ε and K_{f} values were obtained from Eq. (10) using the Newton–Raphson method with the aid of a C-program. Eq. (10) was obtained after some rearrangement of Eq. (5).

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

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

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

where n stands for number of solutions. The standard errors (σ) were 0.159, 0.188, 0.117 and 0.119 in 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 the subscripts. Under the dilute concentration range used, the activity coefficient of the uncharged ligand (f_L) could be assumed to be unity.[28,29] Furthermore, according to Debye–Hückel limiting law $f_\mathrm{M} \approx f_\mathrm{ML}$, and hence the activity coefficients in Eq. (12) cancel each other.[30] The fraction of the total metal ion concentration (α) remaining free at equilibrium could 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. Λ_ML was calculated by a least square linear regression of the data points after the curve (Λ_m *vs.* $c_\mathrm{L}/c_\mathrm{M}$) changes its slope at c_L:c_M ratios (Fig. 4). The next α values were calculated from Eq. (13) for each solution and an initial K_f value for each solution was also calculated using [M] and [L] values. Eq. (12) could also be rearranged as:[31]

$$K_\mathrm{f}[\mathrm{ML}]^2 - \{1 + (c_\mathrm{M} + c_\mathrm{L})K_\mathrm{f}\}[\mathrm{ML}] + K_\mathrm{f} c_\mathrm{M} c_\mathrm{L} = 0 \tag{14}$$

The final K_f values and [ML] were then calculated iteratively using the Newton–Raphson method and successive approximation with the aid of a C-program.[20]

Stability of the complex

The nature of the solvent can strongly influence the stoichiometry of the complex and complexation of transition metal ions in solution. The stability of transition metal complexes with a polydentate ligand depends on several factors such as the number and type of the donor sites present, the number and size of the chelate rings formed on complexation, *etc.*[32] In addition, the stability also

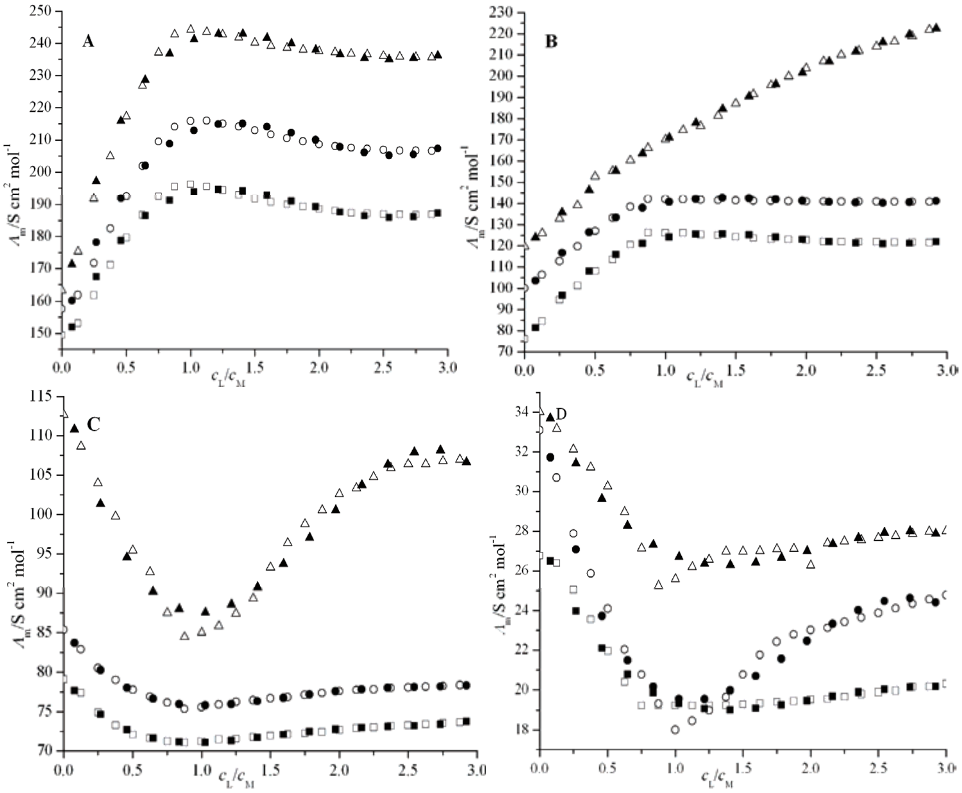

Fig. 4. Molar conductance (Λ_m) *vs*. mole ratio plot (c_L:c_M) for the Cu^{2+}–SAP complex in different solvent mixtures with different mass fractions (w_1) of MeOH at different temperatures: A, w_1 = 1.00; B, w_1 = 0.80; C, w_1 = 0.60; D, w_1 = 0.40. Symbols for the experimental data: □, T = 298.15 K; ○, T = 308.15 K; Δ, T = 318.15 K and symbols for the calculated data (program generated): ■, T = 298.15 K; •, T = 308.15 K; ▲, T = 318.15 K.

depends on the donor strength and the dielectric constants of solvent–solvent mixtures.[33] The molar conductance (Λ_m) *vs*. mole ratio (c_L/c_M) plots are depicted in Fig. 4. Although the ligand solution has negligible conductance, its addition to the metal ion solution when dissolved in pure MeOH and the MeOH–DO mixture with w_1 = 0.80 caused a continuous increase in the molar conductance (Λ_m) up to the mole ratio (c_L:c_M) = 1, except for the solvent mixtures with higher amounts of DO, in which the molar conductance (Λ_m) rather decreased initially on addition of the ligand solution. Such trends in the molar conductance *vs*. mole ratio (c_L/c_M) plots for MeOH rich solvent mixtures is because the complex Cu^{2+}–SAP is more mobile than the free solvated Cu^{2+} and the release of some high-mobility protons and NO_3^- into the solution but for DO rich solvent mixtures, the reversed trend is probably because of the lower dielectric constants and greater solvation of the resulting complex in such solvent mixtures.[34,35] The slope of molar conductivity (Λ_m) *vs.* c_L/c_M plots for all solvent mixtures showed significant changes in slopes when the mole ratio ($c_L:c_M$) was about 1; thus indicating the formation of a relatively stable 1:1 complex (ML) between Cu^{2+} with SAP. From Fig. 4, it is also evident that the curvature of the molar conductivity plots of the Cu^{2+}–SAP complex increased as the temperature increased; this is due to the formation of a comparatively stronger complex at higher temperatures. Therefore, the complexation process between SAP and Cu^{2+} is endothermic. This is also evident from Table I, where it could be seen that the log K_f values for the complex Cu^{2+}–SAP in pure MeOH and in the binary solvent mixtures increased with temperature. However, slightly higher values of log K_f for solvent mixtures with w_1 = 0.80, 0.60 and 0.40 than that of w_1 = 1.00. This is probably due to the enhanced stability of the complex at higher contents of DO and its low dielectric constant.

TABLE I. Values log K_f of Cu^{2+}–SAP complex obtained from conductometric titration in MeOH–DO binary mixtures at different temperatures; standard errors are given in parentheses

w_1	*T* / K		
	298.15	308.15	318.15
1.00	4.69 (±0.11)	4.78 (±0.13)	4.91 (±0.10)
0.80	4.79 (±0.10)	4.94 (±0.14)	5.49 (±0.15)
0.60	4.49 (±0.12)	5.06 (±0.12)	5.09 (±0.12)
0.40	4.57 (±0.16)	4.66 (±0.17)	4.72 (±0.12)

MeOH has a higher Gutmann donor number (*DN* = 19.0) that that of DO (*DN* = 14.8).[36] However, a comparison of the stability constants given in Table I and II revealed that Cu^{2+} was strongly solvated and hardly complexed by the ligand in solvent mixtures with higher content of MeOH and the stability constants increased with increasing the concentration of DO in binary solvents.[20] 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 a solvent plays an important role in complexation reactions. Moreover the stability and selectivity of the formed complexes are affected by a number of molecular factors, such as the number and character of the donor atoms in the Schiff base, the polarisibility and charge density of the metal ion, the nature of the sub-

TABLE II. Values of log K_f for Cu^{2+}–SAP complex obtained from spectrophotometric titration in different binary mixtures of MeOH and DO at 298.15 K; standard errors are given in parentheses

w_1	log K_f
1.00	4.82 (±0.12)
0.80	5.19 (±0.10)
0.60	4.95 (±0.13)
0.40	4.70 (±0.10)

stituents and the character of the co-anion with the cationic species.[37,38] In the Cu^{2+}–SAP complex, the ligand binds the Cu^{2+} through its three binding sites (O, N, O) and the fourth coordination site is most probably occupied by solvent molecules, *i.e.*, MeOH or DO or H_2O molecules.[15,17] The variation of the log K_f of Cu^{2+}–SAP complex as a function of solvent composition (w_1) is shown in Fig. 5 and it showed that the change in the stability constants for Cu^{2+}–SAP complex *vs*. the solvent composition (w_1) was not linear. This evidence reflects that changes might be occurring in the structure of the solvent mixtures[22] and these changes probably alter the solvation 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. Such changes caused changes in the interactions of the solvents with the solutes.[39] It is well known that preferential solvation of ions in mixed solvent systems depends on two factors: the relative donor–acceptor abilities of the 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 solvent–ion interactions for both components.[40]

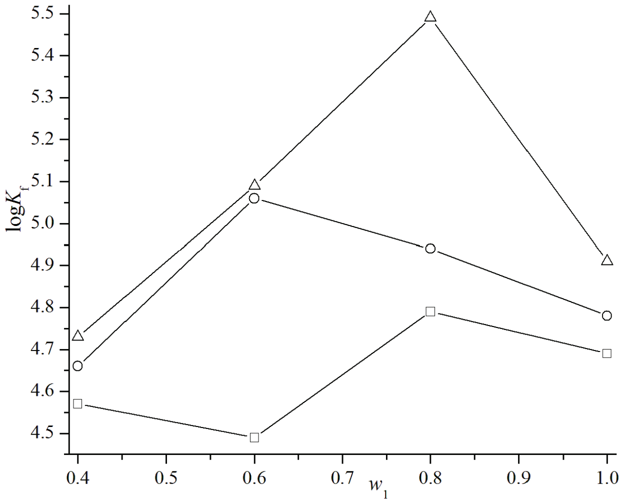

Fig. 5. Variation of the stability constant (log K_f) for the Cu^{2+}–SAP complex against different mass fractions (w_1) of MeOH in the binary solvent mixtures at different temperatures: □, 298.15 K; ○, 308.15 K; Δ, 318.15 K.

Nevertheless, the stability constants given in Tables I and II have nearly same order although the formation constants evaluated by two methods (spectrophotometric and conductometric) were not same but close in magnitude. This is because the experimental data were analysed by two different approaches in the two methods to obtain the stability constants (K_f) and they have their own intrinsic error limit.

Thermodynamic parameters

In order to gain a better understanding of the thermodynamics of the complexation reaction between Cu^{2+} and SAP, it is useful to determine the contribution of enthalpy and entropy of the reaction. The thermodynamic parameters were calculated from the temperature dependence of the complexation constants (Van't Hoff plot shown in Fig. 6):

$$2.303 \log K_f = -\frac{\Delta H}{RT} + \frac{\Delta S}{R} \quad (15)$$

For all the solvent mixtures, 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 various calculated thermodynamic parameters are listed in Table III. The ΔH values associated with the complexation reaction were positive for all the solvent mixtures and the values decreased for the mixed solvents with decreasing the mass fraction of MeOH in the binary solvent mixtures of MeOH with DO. The ΔS values were all always positive and generally decreased with increasing temperature. Moreover, the ΔG values for the present complexation reaction were negative for all the solvents indicating that the reaction was spontaneous and entropy factors were observed to be the dominating factor in making the ΔG values negative. Thus, it is evident that the complexation reactions were spontaneous and entropy-driven in all solvent systems. These trends

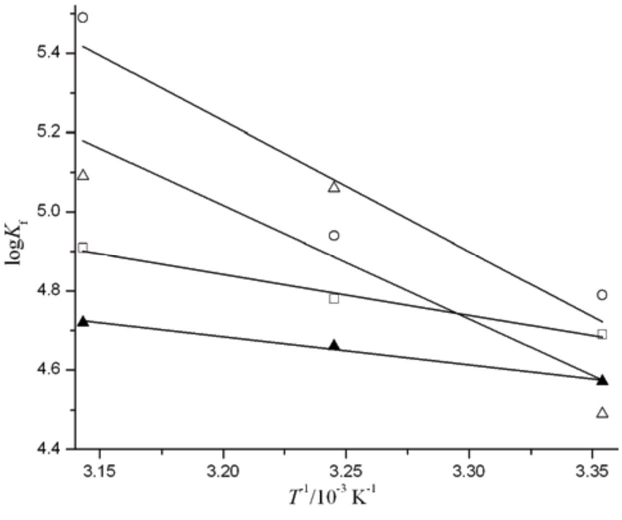

Fig. 6. Van't Hoff Plot for the Cu^{2+}–SAP complex in different solvent mixtures with MeOH mass fractions: □,w_1 = 1.00; w_1 = 0.80 (○), w_1 = 0.60 (Δ) and w_1 = 0.40 (▲).

TABLE III. Thermodynamic parameters (ΔH, ΔS and ΔG) for the formation of the Cu^{2+}–SAP complex in different binary mixtures of MeOH and DO; standard errors are given in parentheses

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	–26.73(±0.12)	–28.29(±0.12)	–29.86(±0.16)	19.93(±0.13)	156.51(±0.19)
0.80	–26.95(±0.21)	–29.98(±0.12)	–33.00(±0.21)	63.15(±0.23)	302.23(±0.13)
0.60	–26.11(±0.13)	–28.83(±0.13)	–31.55(±0.15)	55.00(±0.21)	272.04(±0.21)
0.40	–26.11(±0.12)	–27.44(±0.14)	–28.78(±0.12)	13.65(±0.14)	133.35(±0.15)

are the thermodynamic parameters for the complexation reaction is an overall result of several factors, such as solvation/desolvation of the species involved in the complexation reaction and 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.[41,42] Again electrostatic forces of attraction between two ions of opposite charge depends on the dielectric constants* (ε_r) of the solvents. For the solvents used in this study, ε_r of the solvents decreased as the amount of DO in the solvent mixture increased; thus, addition of DO resulted in a greater attractive force that in effect reduces the dissociation of $Cu(NO_3)_2$ in the solutions and thus the values of log K_f decreased as the amount of DO increased the solvent mixtures.[43] However, a non-linear relation between log K_f and $1/\varepsilon_r$ was found, as shown in Fig 7. Such non-linearity may partly be attributed to preferential solvation of the ionic reactants by one component, in

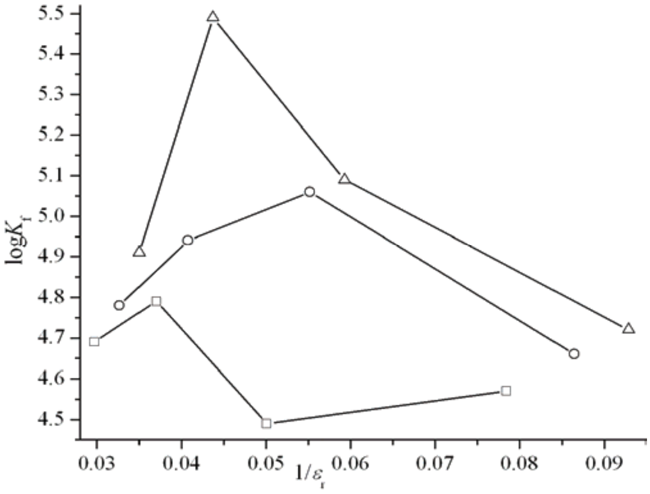

Fig. 7. Plots of the stability constant (log K_f) for the Cu^{2+}–SAP complex against $1/\varepsilon_r$ (ε_r is dielectric constant of the solvent mixtures) at different temperatures; □, 298.15 K; ○, 308.15 K; Δ, 318.15 K.

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* Relative permittivity.

general the more polar component, of the solvent mixture and partly to other solvent properties, such as viscosity, cohesion, hydrogen bonding tendencies and solvolysis propensities, *etc*.[44]

CONCLUSIONS

The stability constants for the complexation of copper(II) ion with *N*-Salicylidene-2-aminophenol (SAP) were determined conductometrically and spectrophotometrically at different temperatures. Thermodynamic parameters of complexation were determined from the temperature dependence of the formation constant. The stoichiometry of the Cu^{2+}–SAP complex in pure MeOH and all MeOH–DO binary mixtures was found to be 1:1. The negative values of ΔG showed the ability of the ligand SAP to form stable complex with Cu^{2+} and the complexation process proceed spontaneously.

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ИЗВОД

СПЕКТРОФОТОМЕТРИЈСКО И КОНДУКТОМЕТРИЈСКО ИСПИТИВАЊЕ КОМПЛЕКСИРАЊА *N*-САЛИЦИЛИДЕН-2-АМИНОФЕНОЛА СА Cu^{2+} У БИНАРНИМ РАСТВОРИМА МЕТАНОЛ + 1,4-ДИОКСАН

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Реакција комплексирања између *N*-салицилиден-2-аминофенола, скраћено SAP, са Cu^{2+} је испитивана у бинарним мешавинама метанола и 1,4-диоксана применом кондуктометријске и спектрофотометријске методе на различитим температурама. Константе стабилности (K_f) за 1:1 комплекс, Cu^{2+}–SAP, су израчунате на основу компјутерског фитовања апсорбанције и моларне проводљивости у функцији различитих молских односа (c_M:c_L или c_L:c_M) у различитим бинарним мешавинама растварача. Нелинерано понашање је опажено у зависности log K_f за комплекс од састава растварача. Различити термодинамички параметри (ΔH, ΔS и ΔG) за форирање Cu^{2+}–SAP комплекса су одређени на основу температурске зависности константе стабилности (K_f). Сви резултати показују да је реакција комплексирања вођена ентропијом и да на њу утиче природа и састав помешаних растварача.

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