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## Solution behaviour of (*N,N'*-ethylenebis(salicylideneiminato))-iron(III) chloride in aqueous methanol at 298.15, 303.15 and 313.15 K

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**Abstract:** In this study partial molar volumes ( $\varphi_V^0$ ) and viscosity *B*-coefficients of (*N,N'*-ethylene-bis(salicylideneiminato))iron(III) chloride, abbreviated as  $\text{Fe}^{\text{III}}(\text{salen})\text{Cl}$ , in different aqueous methanolic solutions were determined from solution density and viscosity measurements at the temperatures 298.15, 303.15, and 313.15 K under ambient pressure. The apparent molar volumes ( $\varphi_V$ ) and densities ( $\rho$ ) were used to calculate the apparent molar expansibilities ( $\varphi_E$ ), the partial molar expansibilities ( $\varphi_E^0$ ) and the temperature dependence of the partial molar expansibilities ( $\varphi_E^0$ ) at constant pressure,  $(\partial\varphi_E^0/\partial T)_p$  of  $\text{Fe}^{\text{III}}(\text{salen})\text{Cl}$  solutions to reveal the nature of different interactions in the ternary solutions. The transition state theory was applied to analyze the viscosity *B*-coefficients based on the activation parameters of viscous flow. The overall results indicated strong solute–solvent interactions between  $\text{Fe}^{\text{III}}(\text{salen})\text{Cl}$  and the solvent molecules, preferentially with water molecules and that  $\text{Fe}^{\text{III}}(\text{salen})\text{Cl}$  acts as a net structure promoter in the ternary solutions. The UV–Vis absorption spectra of the ternary solutions stand in support of the obtained results.

**Keywords:** partial molar volumes; viscosity *B*-coefficients; (*N,N'*-ethylene-bis(salicylideneiminato))iron(III) chloride; aqueous methanol.

### INTRODUCTION

Many natural products contain structural units similar to those of metal heterocyclic compounds that could be used as targets for synthetic, methodological, and biological applications.<sup>1</sup> Schiff base metal complexes belong to class of the many potential materials that deserve extensive studies and, amongst the traditional metal complexes, salen-type Schiff base ligands or their derivatives are of great importance in coordination chemistry and homogeneous catalysis.<sup>2</sup> They can also be regarded as models of reaction centres for metalloenzymes<sup>3</sup> and

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nonlinear optical materials.<sup>4</sup> According to Groves *et al.*,<sup>5–7</sup> simple iron(III) porphyrins can be used as models for the reaction site of cytochrome P-450. In this regard, metal complexes of the salen ligand are also of great interest to synthetic chemists, since they share features in common with metalloporphyrins as far as their electronic structure and catalytic activities are concerned. Interestingly, Fe<sup>III</sup>(salen)Cl and Fe<sup>III</sup> porphyrins have some structural and chemical similarities.<sup>8,9</sup> Like Fe<sup>III</sup> porphyrins, the iron atom of Fe<sup>III</sup>(salen)Cl has a penta-coordinated pyramidal geometry wherein the tetradentate salen ligand is in a square planar coordination and the chloride ligand is attached at an apical position. The complex has an open sixth coordination site and salen forms some complexes that mimic porphyrin chemistry.<sup>10</sup> Moreover, Fe<sup>III</sup>(salen)Cl has an affinity for oxygen molecules and is capable of forming oxo-species as do Fe<sup>III</sup> porphyrin derivatives.<sup>8,9</sup> Amongst the conventional solvents, methanol is used in numerous chemical processes and it has a structure analogous to water but with a –CH<sub>3</sub> group in place of a proton. This substitution affects the liquid structure and causes significant differences between methanol and water. Hence it is important to understand how solutes such as Fe<sup>III</sup>(salen)Cl behave in these mixed methanol–water solvents, because an understanding of such behaviour could throw light on the effects of solute concentration on the hydrogen-bonded network, solvation structure and solute dynamics, *etc.*<sup>11</sup>

However, such studies on Fe<sup>III</sup>(salen)Cl in various pure and mixed solvents are still rare in the literature. To the best of our knowledge, only one report on the solvent effects on the electrochemical behaviour of Fe<sup>III</sup>(salen)Cl is available in the literature.<sup>12</sup> Hence in this work, the solution behaviour of Fe<sup>III</sup>(salen)Cl in different aqueous methanol solutions were studied at 298.15, 303.15 and 313.15 K under ambient pressure and the results are discussed in terms of solute–solute and solute–solvent interactions.

## EXPERIMENTAL

### Materials

Analytical reagent (AR) grade ferric chloride, FeCl<sub>3</sub>·6H<sub>2</sub>O (s), 1,2-ethylenediamine (l), and salicylaldehyde (l), each of purity > 99 %, were purchased from Merck, India. These chemicals were used as received. Spectroscopic grade methanol (minimum assay, GC, purity > 99.8 %) with 0.05 % of water was purchased from Merck, India and used as received. Doubly distilled de-ionized water with a specific conductance of 1×10<sup>-6</sup> S cm<sup>-1</sup> at 298.15 K was used for preparing the mixed solvents. Various binary solvents were prepared by mass, with necessary adjustments by volume, to achieve the exact mass fraction of methanol ( $w_1 = 0.60, 0.70, 0.80$  and  $0.90$ ) at 298.15 K. The relative error in solvent composition was estimated to be about 1 %. The physical properties of different solvent/solvent mixtures at the experimental temperatures are reported in Table S-I of the Supplementary material to this paper and compared against available literature values.<sup>13–16</sup>

Fe<sup>III</sup>(salen)Cl was prepared by a known method<sup>17</sup> taking FeCl<sub>3</sub>·6H<sub>2</sub>O(s) and the Schiff base, salenH<sub>2</sub>(s) in ethanol (in a 1:1 molar ratio). SalenH<sub>2</sub> (*N,N'*-ethylenebis(salicylidene-

amine)) was obtained from an ethanolic solution of 1,2-ethylenediamine and salicylaldehyde (in a 1:2 molar ratio) for 1 h. The bright yellow crystalline solid (m.p. 128 °C) was filtered and washed with ethanol several times and dried under vacuum. Metallation was realized by refluxing an ethanolic solution containing  $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$  (s) (1.08 g, 4 mmol) and  $\text{salenH}_2$  (1.07 g, 4 mmol) with little triethylamine ( $\text{NEt}_3$ ) for 30 min at 60 °C.  $\text{Fe}^{\text{III}}(\text{salen})\text{Cl}$  was obtained as a deep brown microcrystalline solid from the mixture and was dried under vacuum at 50–60 °C and then recrystallized from ethanol. It was kept in a vacuum desiccator over anhydrous  $\text{CaCl}_2$ . The purity of the complex was checked by elemental analysis (Calcd.: C, 53.74; H, 3.95; N, 7.84; Cl, 9.91; Fe, 15.63 %. Found: C, 53.64; H, 4.01; N, 7.94; Cl, 9.85; Fe, 15.60 %) and IR spectroscopy. Elemental micro-analyses were realised with the aid of a Perkin–Elmer (Model 240C) instrument. The IR spectra were recorded on a Perkin–Elmer FT-IR spectrophotometer. Characteristic IR bands for the prepared complex (KBr,  $\text{cm}^{-1}$ ) are 585.76, 617.44, 757.92, 795.02, 904.87, 1445.82, 1544.35, 1629.76, 3448.17. The magnetic moment (measured with a Sherwood Scientific magnetic balance) was found to be  $5.31 \mu_{\text{B}}$  ( $5.29 \mu_{\text{B}}^{18}$ ) at room temperature. The molecular structures of the ligand  $\text{SalenH}_2$ , the complex  $\text{Fe}^{\text{III}}(\text{salen})\text{Cl}$  and its dimer  $[\text{Fe}^{\text{III}}(\text{salen})\text{Cl}]_2$  are illustrated in Fig. S-1 of the Supplementary material. The IR spectra of the ligand  $\text{SalenH}_2$  and  $\text{Fe}^{\text{III}}(\text{salen})\text{Cl}$  are shown in Fig. S-2 of the Supplementary material.

Stock solutions of the complex in different aqueous methanol solutions were prepared by mass and the working solutions were prepared by mass dilution. Solute molalities ( $m$ ) were converted into molarities ( $c$ ) using experimental density values. All solutions were prepared fresh and degassed with dry nitrogen before use. The uncertainty in the molarity of  $\text{Fe}^{\text{III}}(\text{salen})\text{Cl}$  solutions was evaluated to be  $\pm 0.0001 \text{ mol dm}^{-3}$ .

#### Methods

The mass measurements were performed on a digital electronic analytical balance (Mettler, AG 285, Switzerland) with a precision of  $\pm 0.01 \text{ mg}$ . The densities were measured with a vibrating-tube density meter (Anton Paar, DMA 4500M), which was calibrated at the experimental temperatures with doubly distilled, degassed water and dry air at atmospheric pressure. The temperature was automatically kept constant with an accuracy of  $\pm 1 \times 10^{-3} \text{ K}$  using a built-in Peltier device. The stated repeatability and accuracy of the densities were  $\pm 1 \times 10^{-5}$  and  $\pm 5 \times 10^{-5} \text{ g cm}^{-3}$ , respectively. However, when the accuracy of the measured densities was checked with the density of an aqueous NaCl solution of known molality based on the data given by Pitzer,<sup>19</sup> the uncertainty of the measured densities for most of the solutions was estimated to be  $\pm 1 \times 10^{-5} \text{ g cm}^{-3}$ . The viscosity was measured by means of a suspended Ubbelohde (Canon-type) viscometer thoroughly cleaned, dried and calibrated at the experimental temperatures with triply distilled, degassed water and purified methanol.<sup>20–22</sup> It was filled with experimental solution and placed vertically in a glass sided thermostat (maintained constant to  $\pm 0.01 \text{ K}$ ) with the aid of wooden clumps. Sufficient time was allowed for the attainment of thermal equilibrium and the flow times of the solutions were recorded with a digital stopwatch (correct to  $\pm 0.01 \text{ s}$ ). In all determinations, adequate precautions were taken to minimize evaporation losses and at least three repetitions of each data (reproducible to  $\pm 0.02 \text{ s}$ ) were taken as the average of the flow times. The uncertainty in viscosity measurements was estimated to be within  $\pm 4 \times 10^{-4} \text{ mPa s}$ . The absorption spectra of  $\text{Fe}^{\text{III}}(\text{salen})\text{Cl}$  ( $5 \times 10^{-5} \text{ mol dm}^{-3}$ ) in different aqueous methanol solutions at 298.15 K were recorded on Jasco V-530 double beam UV–Vis spectrophotometer (coupled with a thermostatic arrangement). A quartz cell with a path length of 1 cm was used and the reference solvent was spectroscopic grade methanol for all the spectroscopic measurements.

## RESULTS AND DISCUSSION

Molalities ( $m$ ), densities ( $\rho$ ) viscosities ( $\eta$ ) and the apparent molar volumes ( $\varphi_V$ ) for the experimental solutions of  $\text{Fe}^{\text{III}}(\text{salen})\text{Cl}$  in different aqueous methanol solutions at various temperatures are given in Table S-II of the Supplementary material. The apparent molar volumes ( $\varphi_V$ ) of  $\text{Fe}^{\text{III}}(\text{salen})\text{Cl}$  in different aqueous methanol solutions were determined from the solution densities by using the following equation:

$$\varphi_V = (M / \rho_1) - 1000(\rho - \rho_1) / (m\rho\rho_1) \quad (1)$$

where  $M$  is the molar mass of  $\text{Fe}^{\text{III}}(\text{salen})\text{Cl}$ ,  $m$  is the molality of the solution,  $\rho_1$  and  $\rho$  are the densities of the solvent and solution, respectively. When the  $\varphi_V$  values were plotted against the square root of molal concentrations ( $\sqrt{m}$ ), a linear dependence was observed. Hence the partial molar volumes ( $\varphi_V^0$ ) at infinite dilution and the experimental slopes ( $S_V^*$ ) were determined using the least squares fitting of  $\varphi_V$  values to the Masson Equation:<sup>23</sup>

$$\varphi_V = \varphi_V^0 + S_V^* \sqrt{m} \quad (2)$$

The  $\varphi_V^0$  and  $S_V^*$  values are reported in Table I, which shows that the  $\varphi_V^0$  values are positive and increase as the amount of water in the mixtures increases

TABLE I. Partial molar volumes ( $\varphi_V^0$ ) and the slopes ( $S_V^*$ ) of Eq. (2) with the corresponding standard deviations ( $\sigma$ ) for  $\text{Fe}^{\text{III}}(\text{Salen})\text{Cl}$  in different aqueous methanol solutions at different temperatures (standard errors are given in parenthesis);  $w_1$  – mass fraction of methanol

$T / \text{K}$	$\varphi_V^0 \times 10^6 / \text{m}^3 \text{mol}^{-1}$	$S_V^* \times 10^6 / \text{m}^3 \text{kg}^{1/2} \text{mol}^{-3/2}$	$\sigma \times 10^6 / \text{m}^3 \text{mol}^{-1}$
$w_1 = 1.00$			
298.15	247.37 ( $\pm 4.65$ )	-1537.95 ( $\pm 56.44$ )	3.10
303.15	228.45 ( $\pm 4.26$ )	-1400.29 ( $\pm 51.76$ )	2.84
313.15	216.30 ( $\pm 5.18$ )	-1335.03 ( $\pm 62.88$ )	3.45
$w_1 = 0.90$			
298.15	257.09 ( $\pm 5.83$ )	-1659.90 ( $\pm 72.09$ )	3.86
303.15	243.14 ( $\pm 3.17$ )	-1554.86 ( $\pm 39.15$ )	2.10
313.15	232.10 ( $\pm 4.65$ )	-1524.93 ( $\pm 57.44$ )	3.08
$w_1 = 0.80$			
298.15	260.72 ( $\pm 4.47$ )	-1779.20 ( $\pm 56.26$ )	2.96
303.15	253.03 ( $\pm 0.02$ )	-1734.17 ( $\pm 50.46$ )	2.66
313.15	244.78 ( $\pm 3.02$ )	-1672.77 ( $\pm 38.05$ )	2.00
$w_1 = 0.70$			
298.15	262.39 ( $\pm 3.59$ )	-1830.54 ( $\pm 45.76$ )	2.39
303.15	257.29 ( $\pm 3.95$ )	-1799.56 ( $\pm 50.35$ )	2.63
313.15	256.91 ( $\pm 3.95$ )	-1826.92 ( $\pm 50.39$ )	2.63
$w_1 = 0.60$			
298.15	264.36 ( $\pm 5.07$ )	-1912.71 ( $\pm 65.74$ )	3.40
303.15	261.07 ( $\pm 6.86$ )	-1917.72 ( $\pm 88.93$ )	4.60
313.15	261.20 ( $\pm 4.89$ )	-1931.27 ( $\pm 63.41$ )	3.28

but decrease with increasing temperature. This indicates the presence of strong solute–solvent interactions<sup>22,24</sup> and these interactions were further strengthened at higher contents of water but weakened at higher temperatures. The dependences of the  $\varphi_V^0$  values on the solvent composition and temperature are shown in Fig. 1.  $\text{Fe}^{\text{III}}(\text{salen})\text{Cl}$  can exist either as dimer or monomer in the solid state. Its behaviour in the solid state depends on the nature of the solvent used in its recrystallization. However, the two forms can be distinguished by their magnetic moments and IR spectra (shown in Fig. S-2 of the Supplementary material). For monomeric complexes, the range of the magnetic moment is 5.29–6.06  $\mu_B$ . A value of 5.31  $\mu_B$  was obtained for the complex  $\text{Fe}^{\text{III}}(\text{salen})\text{Cl}$  and the IR spectra are devoid of any band near 850  $\text{cm}^{-1}$ . Thus, the complex was in monomeric form<sup>25</sup> rather than in the dimeric form and hence, it contains a  $d^5$  high spin electronic configuration<sup>26,27</sup> with a square planar geometry around  $\text{Fe}^{3+}$  at the centre and an apical chlorine atom as coordinated to the fifth coordination site. Thus, solvent molecules can coordinate to the unoccupied sixth position of the coordination site. In this regard, the donor power of individual solvents plays a crucial role. Aqueous methanol solutions are characterized by hydrophobic and hydrophilic interactions. Both computer simulation<sup>28</sup> and experimental studies<sup>29–34</sup> revealed that water strongly interacts with methanol to form complexes. Recent spectroscopic and high performance liquid chromatographic studies revealed that methanol forms a number of complexes with a number of water molecules at low methanol but at high methanol content, it forms a 1:1 complex.<sup>29–34</sup> According to Zhang and Wu,<sup>35</sup> the two critical solvent compositions are  $\text{H}_2\text{O}:\text{CH}_3\text{OH} \approx 5:1$  and  $\approx 1:1$ . Thus, as the methanol concentration decreases, more water molecules become free in the bulk solvent mixtures. Hence methanol and water molecules may coordinate for the sixth vacant coordination site of  $\text{Fe}^{\text{III}}(\text{salen})\text{Cl}$  via  $\text{O}\cdots\text{Fe}$  interactions. Moreover, methanol/water may also interact with  $\text{Fe}^{\text{III}}(\text{salen})\text{Cl}$  via hydrogen bond interactions with ONNO sites of the complex and thereby affecting its spin-equilibrium in solution. No doubt,  $\text{H}_2\text{O}$  will have comparatively more such hydrogen bond interactions than  $\text{CH}_3\text{OH}$  and because of the fact that methanol (with an effective hard sphere diameter 0.364  $\text{nm}^{36}$ ) is more bulky than water (with effective hard sphere diameter 0.284  $\text{nm}^{36}$ ), the increase in the  $\varphi_V$  values as well as the concomitant increase in the  $\varphi_V^0$  values with increasing water content in the mixtures may be attributed to preferential coordination of the unoccupied sixth position of  $\text{Fe}^{\text{III}}(\text{salen})\text{Cl}$  by water molecules or preferential solvation of  $\text{Fe}^{\text{III}}(\text{salen})\text{Cl}$  by water molecules due to stronger electrostatic interaction and comparatively more donor strength of water than methanol.<sup>37</sup> Again, as the  $\varphi_V^0$  values for the ternary systems increase with more water or polarity of the solvent mixture (the order of relative permittivity of the solvent mixtures:<sup>24</sup> 31.5, 35.7, 40.1, 45.0 and 50.1 for  $w_1 = 1.00, 0.90, 0.80, 0.70$  and 0.60, respectively), the complex most probably remains in its monomeric form in the

solution phase, because the Fe-atom is comparatively more available to the solvent molecules for O $\cdots$ Fe interactions in the monomeric form<sup>18</sup> than in the dimeric form. However, the decrease in the  $\phi_V^0$  values with rising temperature indicates disruption of hydrogen bonds and O $\cdots$ Fe interactions at elevated temperatures. The slight increase in the  $\phi_V^0$  values at 303.15 and 313.15 K for solvent mixtures with  $w_1 = 0.60$  may probably arise from a delicate balance between the loosely bound dimer and the monomer in this solvent compositions.<sup>25,27</sup> The parameter  $S_V^*$  is a volumetric virial coefficient and characterizes the pair-wise interactions between solvated species<sup>38,39</sup> in solution. Its sign is determined by the interactions between solute species (solute–solute interactions). The negative values of  $S_V^*$  and their trend opposite to that of the  $\phi_V^0$  values indicate weak solute–solute interactions for Fe<sup>III</sup>(salen)Cl in the studied experimental aqueous methanol solutions.

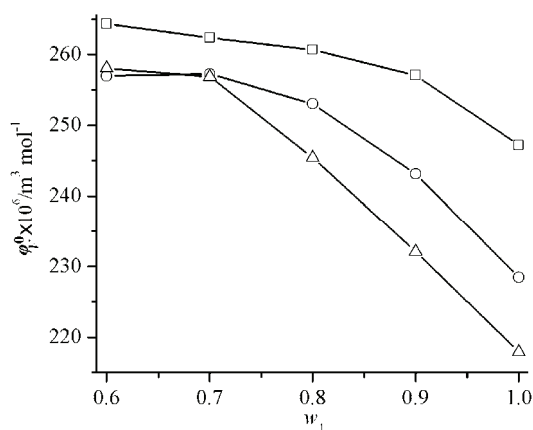


Fig. 1. Dependence of partial molar volume ( $\phi_V^0$ ) on the mass fraction of methanol ( $w_1$ ) in the aqueous methanol solutions at different temperatures. Symbols:  $T = 298.15$  K,  $\square$ ;  $T = 303.15$  K,  $\circ$ ;  $T = 313.15$  K,  $\Delta$ .

These results are reflected in the UV–Vis absorption spectra of the studied solutions. The absorption spectra of the Schiff base, salenH<sub>2</sub> in methanol and various aqueous methanol solutions at 298.15 K are shown in Fig. 2. The spectrum of salenH<sub>2</sub> in methanol is characterized by the presence of two strong peaks at 254 and 316 nm and a weak peak at 404 nm, which were discussed previously.<sup>22</sup> Interestingly, when water was introduced, the peak at 404 nm of salenH<sub>2</sub> gradually disappeared and a valley was formed as the concentration of water increased in the ternary solutions and thus, the position of the weak peak at 404 nm varies with the polarity of the aqueous methanol solutions. In addition, the 316 nm peak underwent hypochromic shifts on addition of water. The absorption spectra of Fe<sup>III</sup>(salen)Cl in methanol and various aqueous methanol solutions at 298.15 K are shown in Fig. 3, which shows that the 404 nm peak of the Schiff base disappeared in methanol as well as in all the aqueous methanol solutions due to coordination of solvent molecules to Fe(III). Simultaneously, an additional

peak at around 500 nm appeared and suffered hypsochromic shifts, indicating coordination or solvation by solvent molecules.<sup>40</sup> The peak at 258 nm did not change appreciably but a new peak at around 320 nm appeared as the amount of water in the ternary systems increased.<sup>27</sup>

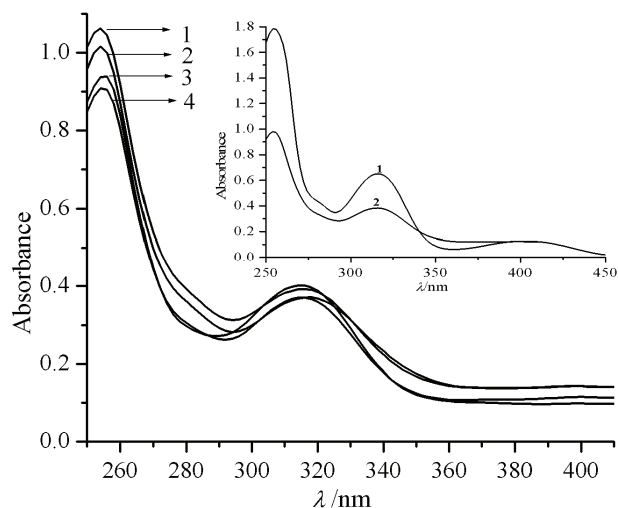


Fig. 2. Changes in the UV-Vis absorption spectra of  $\text{salenH}_2$  solutions in different aqueous methanol solutions at 298.15 K for  $w_1$ : 1, 0.70; 2, 0.60; 3, 0.90; 4, 0.80.  $w_1$  is the mass fraction of methanol in the aqueous methanol solutions. Inset: 1,  $\text{salenH}_2$  in methanol; 2, average absorption spectra in aqueous methanol mixtures at 298.15 K.

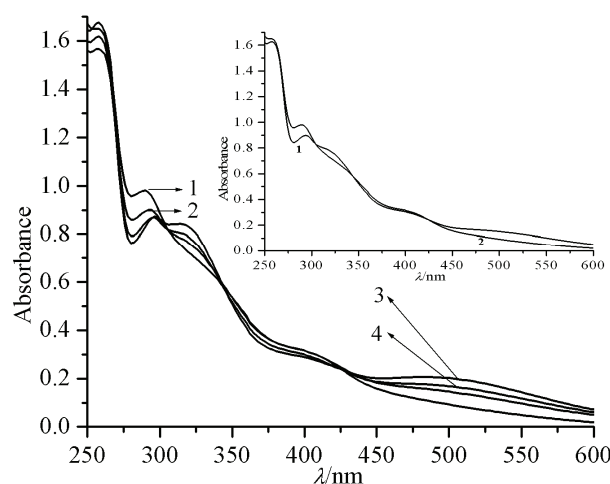


Fig. 3. Changes in the UV-Vis absorption spectra of  $\text{Fe}^{\text{III}}(\text{salen})\text{Cl}$  solutions in different aqueous methanol solutions at 298.15 K for  $w_1$ : 1, 1.00; 2, 0.90; 3, 0.70; 4, 0.80.  $w_1$  is the mass fraction of methanol in the aqueous methanol solutions. Inset: 1,  $\text{Fe}^{\text{III}}(\text{salen})\text{Cl}$  in methanol; 2, average absorption spectra in aqueous methanol mixtures at 298.15 K.



The apparent molar volumes ( $\varphi_V$ ) and densities ( $\rho$ ) were used to derive the apparent molar expansibilities ( $\varphi_E$ ) of  $\text{Fe}^{\text{III}}(\text{salen})\text{Cl}$  solutions by using the relation:<sup>24</sup>

$$\varphi_E = \alpha\varphi_V + 1000(\alpha - \alpha_0) / (m\rho_0) \quad (3)$$

where  $\alpha$  and  $\alpha_0$  are the coefficients of isobaric thermal expansion of the solvent and solution, respectively, and the other symbols have their usual significances;  $\alpha$  and  $\alpha_0$  are defined as:  $\alpha = -\rho_0^{-1}(\delta\rho_0/\delta T)_p$  and  $\alpha_0 = -\rho^{-1}(\delta\rho/\delta T)_p$ , respectively. The uncertainty of the  $\alpha$  and  $\alpha_0$  values was  $\pm 6 \times 10^{-6} \text{ K}^{-1}$  and the uncertainty in the  $\varphi_E$  values was within  $\pm(0.006-0.061) \times 10^{-6} \text{ m}^3 \text{ mol}^{-1} \text{ K}^{-1}$ . The partial molar expansibilities ( $\varphi_V^0$ ) were determined from the relation:<sup>24</sup>

$$\varphi_E = \varphi_E^0 + S_E \sqrt{m} \quad (4)$$

The  $\varphi_E^0$  values for the different experimental solutions at different temperatures are listed in Table S-III of the Supplementary material. The Table reveals that the  $\varphi_E^0$  values are negative and decrease further as the temperature increases but increase with increasing content of  $\text{H}_2\text{O}$  for all the solutions. These facts may be attributed to structural perturbation influenced by the gradual appearance or disappearance of the caging/packing effect<sup>41</sup> as the water content increases in the ternary solutions or as the temperature of the solutions increases, respectively.

According to Hepler,<sup>42</sup> the sign of  $(\delta\varphi_E^0/\delta T)_p$  is a better criterion in characterizing the long-range structure making or breaking ability of a solute in the solution phase. If the  $(\delta\varphi_E^0/\delta T)_p$  values are small negative or positive, the solute acts as a structure maker, otherwise it acts as a structure breaker. The  $(\delta\varphi_E^0/\delta T)_p$  values were obtained from the slope of a linear fit of the  $\varphi_E^0$  values against the experimental temperature ( $T$ ). The correlation coefficients ( $R^2$ ) values were within the range (0.97210–0.99552). The  $(\delta\varphi_E^0/\delta T)_p$  values for different ternary solutions are given in Table S-III of the Supplementary material and  $\text{Fe}^{\text{III}}(\text{salen})\text{Cl}$  was found to act as a net structure promoter in the aqueous methanol solutions.

It is reported<sup>43</sup> that  $\text{Fe}^{\text{III}}(\text{salen})\text{Cl}$  can produce a stable  $[\text{Fe}^{\text{III}}(\text{salen})]^+$  cation but the experimental solutions did not respond to the  $\text{AgNO}_3$  test for free  $\text{Cl}^-$ . Hence, the solution viscosities ( $\eta$ ) were analysed with a modified Jones–Dole equation:<sup>44</sup>

$$\eta/\eta_1 = \eta_r = 1 + Bc \quad (5)$$

where  $\eta_r = \eta/\eta_1$  is the relative viscosity;  $\eta_1$  and  $\eta$  are the viscosities of solvent and solution, respectively. The adjustable parameter  $B$ , referred to as the viscosity  $B$ -coefficient, was obtained by least squares analysis and the obtained values are reported in Table II. Similar to  $\varphi_V^0$ , the viscosity  $B$ -coefficient<sup>45,46</sup> provides another avenue to the effects of solute–solvent interactions based on the solution viscosity. Table II shows that the viscosity  $B$ -coefficients for  $\text{Fe}^{\text{III}}(\text{salen})\text{Cl}$  in the



studied solvent systems were positive but their temperature dependence was negative. A solute that has positive viscosity  $B$ -coefficients with a negative dependence on temperature is generally considered as a structure maker. Accordingly  $\text{Fe}^{\text{III}}(\text{salen})\text{Cl}$  can be considered as a structure maker for the present solvent systems studied. However, the viscosity  $B$ -coefficients decreased on the introduction of water ( $w_1$  from 1.00 to 0.90), but after that the viscosity  $B$ -coefficients increased monotonically with further addition of water to the ternary solutions. This is probably due to a sudden perturbation of the arrangement of methanol molecules in the bulk methanol structure arising from strong solvent–solvent interactions in the solvent mixture with  $w_1 = 0.90$ . However, for the remaining solvent compositions, solute–solvent interaction seems to dominate in the characterisation of the solution viscosities and the viscosity  $B$ -coefficients.

TABLE II. Viscosity  $B$ -coefficients with standard deviations ( $\sigma$ ) for  $\text{Fe}^{\text{III}}(\text{salen})\text{Cl}$  in different aqueous methanol solutions for linear regression of Eq. (5) at different temperatures (standard errors are given in parenthesis);  $w_1$  – mass fraction of methanol

Parameter	$T / \text{K}$		
	298.15	303.15	313.15
$w_1 = 1.00$			
$B \times 10^3 / \text{m}^3 \text{mol}^{-1}$	8.424 ( $\pm 0.254$ )	8.255 ( $\pm 0.161$ )	8.124 ( $\pm 0.143$ )
$R^2$	0.99459	0.99772	0.99815
$\sigma \times 10^3$	0.002	0.001	0.001
$w_1 = 0.90$			
$B \times 10^3 / \text{m}^3 \text{mol}^{-1}$	7.295 ( $\pm 0.156$ )	6.941 ( $\pm 0.265$ )	6.706 ( $\pm 0.124$ )
$R^2$	0.99725	0.99131	0.99794
$\sigma \times 10^3$	0.001	0.002	0.001
$w_1 = 0.80$			
$B \times 10^3 / \text{m}^3 \text{mol}^{-1}$	7.649 ( $\pm 0.180$ )	7.123 ( $\pm 0.244$ )	6.887 ( $\pm 0.199$ )
$R^2$	0.99667	0.99302	0.99502
$\sigma \times 10^3$	0.001	0.002	0.001
$w_1 = 0.70$			
$B \times 10^3 / \text{m}^3 \text{mol}^{-1}$	7.883 ( $\pm 0.364$ )	7.193 ( $\pm 0.004$ )	6.991 ( $\pm 0.079$ )
$R^2$	0.98738	0.99999	0.99922
$\sigma \times 10^3$	0.002	0.001	0.001
$w_1 = 0.60$			
$B \times 10^3 / \text{m}^3 \text{mol}^{-1}$	7.891 ( $\pm 0.231$ )	7.439 ( $\pm 0.261$ )	7.133 ( $\pm 0.298$ )
$R^2$	0.99490	0.99265	0.98962
$\sigma \times 10^3$	0.002	0.002	0.002

According to Eyring and co-workers,<sup>46</sup> the application of statistical thermodynamics to the hole model of viscous flow based on the absolute reaction rate theory yielded the following relation for the free energy of activation for viscous flow per mole of the solvent/solvent mixture ( $\Delta\mu_1^{\ominus*}$ ):

$$\Delta\mu_1^{\ominus*} = \Delta G_1^{\ominus*} = RT \ln \left( \frac{\eta_1 \phi_{V,1}^0}{hN_A} \right) \quad (6)$$

where  $N_A$  and  $\phi_{V,1}^0$  are the Avogadro number and the partial molar volumes of the solvent, respectively. Other symbols have their usual meanings.<sup>45</sup> The above relation was also used for liquid mixtures<sup>45,46</sup> and when rearranged this relation can be expressed as:

$$RT \ln \left( \frac{\eta_1 \phi_{V,1}^0}{hN_A} \right) = - \left( \frac{\Delta S_1^{\ominus*}}{R} \right) + \left( \frac{\Delta H_1^{\ominus*}}{R} \right) \left( \frac{1}{T} \right) \quad (7)$$

Hence, the values of  $\Delta H_1^{\ominus*}$  and  $\Delta S_1^{\ominus*}$  were obtained from a linear regression treatment of Eq. (7) with correlation coefficient ( $R^2$ ) values within the range 0.99866–0.99961. Plots of  $\ln (\eta_1 \phi_{V,1}^0 / hN_A)$  against  $(10^3/T)$  are shown in Fig. S-3 of the Supplementary material. A correlation between viscosity  $B$ -coefficients and the deviation between the contribution per mole of a solute to the free energy of activation for viscous flow of the solution ( $\Delta\mu_2^{\ominus*}$ ) and the free energy of activation of viscous flow per mole of the pure solvent or solvent mixture ( $\Delta\mu_1^{\ominus*}$ ) was suggested by Feakins *et al.*,<sup>47</sup> in the form of the following relation:

$$B = (v\phi_{V,1}^0 - \phi_{V,2}^0) + \phi_{V,1}^0 \frac{(\Delta\mu_2^{\ominus*} - v\Delta\mu_1^{\ominus*})}{RT} \quad (8)$$

where the coefficient  $v$  is 1 for an undissociated uncharged solute and  $\phi_{V,2}^0$  is the partial molar volume of the solute. Thus, the  $(\Delta\mu_2^{\ominus*} - \Delta\mu_1^{\ominus*})$  values were calculated using relation (8) and the  $B$ -coefficient values were obtained from Eq. (5). Again, the  $(\Delta\mu_2^{\ominus*} - \Delta\mu_1^{\ominus*})$  values can also be expressed as:

$$\frac{(\Delta\mu_2^{\ominus*} - \Delta\mu_1^{\ominus*})}{RT} = - \frac{(\Delta S_2^{\ominus*} - \Delta S_1^{\ominus*})}{R} + \left[ \frac{(\Delta H_2^{\ominus*} - \Delta H_1^{\ominus*})}{R} \right] \left( \frac{1}{T} \right) \quad (9)$$

where  $\Delta S_i^{\ominus*}$  and  $\Delta H_i^{\ominus*}$  are the standard partial molar entropy and enthalpy, respectively, of activation for viscous flow per mole of  $i^{\text{th}}$  component in the solution. Hence, a linear regression treatment of Eq. (9), with the correlation coefficient ( $R^2$ ) values within the range 0.81698–0.96863, provided the values of  $(\Delta S_2^{\ominus*} - \Delta S_1^{\ominus*})$  and  $(\Delta H_2^{\ominus*} - \Delta H_1^{\ominus*})$  from the corresponding slopes and intercept. The parameters  $\Delta\mu_1^{\ominus*}$  and  $(\Delta\mu_2^{\ominus*} - \Delta\mu_1^{\ominus*})$  are reported in Table III.  $\Delta H_1^{\ominus*}$ ,  $(\Delta H_2^{\ominus*} - \Delta H_1^{\ominus*})$ ,  $\Delta S_1^{\ominus*}$  and  $(\Delta S_2^{\ominus*} - \Delta S_1^{\ominus*})$  are reported in Table IV. Plots of  $(\Delta\mu_2^{\ominus*} - \Delta\mu_1^{\ominus*}) / RT$  against  $(10^3/T)$  are shown in Fig. S-4 of the Supplementary material.

TABLE III. The free energy of activation for viscous flow per mole of the solvent–solvent mixture,  $\Delta\mu_1^{\ominus*}$ , its deviation from the free energy of activation for viscous flow per mole of the solute,  $\Delta\mu_2^{\ominus*}$ , and  $(\Delta\mu_2^{\ominus*} - \Delta\mu_1^{\ominus*})$  for Fe<sup>III</sup>(salen)Cl in different aqueous methanol solutions at different temperatures (standard errors are given in parenthesis);  $w_1$  – mass fraction of methanol

$T / \text{K}$	$\Delta\mu_1^{\ominus*} / \text{kJ mol}^{-1}$	$(\Delta\mu_2^{\ominus*} - \Delta\mu_1^{\ominus*}) / \text{kJ mol}^{-1}$
$w_1 = 1.00$		
298.15	9.97 ( $\pm 0.01$ )	525.22 ( $\pm 0.26$ )
303.15	9.97 ( $\pm 0.01$ )	519.26 ( $\pm 0.17$ )
313.15	10.00 ( $\pm 0.01$ )	521.15 ( $\pm 0.15$ )
$w_1 = 0.90$		
298.15	10.52 ( $\pm 0.01$ )	511.29 ( $\pm 0.16$ )
303.15	10.53 ( $\pm 0.01$ )	491.39 ( $\pm 0.27$ )
313.15	10.61 ( $\pm 0.01$ )	484.95 ( $\pm 0.13$ )
$w_1 = 0.80$		
298.15	10.95 ( $\pm 0.01$ )	593.23 ( $\pm 0.18$ )
303.15	11.04 ( $\pm 0.01$ )	559.14 ( $\pm 0.25$ )
313.15	11.22 ( $\pm 0.01$ )	553.04 ( $\pm 0.20$ )
$w_1 = 0.70$		
298.15	11.12 ( $\pm 0.01$ )	671.90 ( $\pm 0.37$ )
303.15	11.23 ( $\pm 0.01$ )	621.36 ( $\pm 0.01$ )
313.15	11.43 ( $\pm 0.01$ )	618.75 ( $\pm 0.08$ )
$w_1 = 0.60$		
298.15	11.33 ( $\pm 0.01$ )	734.73 ( $\pm 0.24$ )
303.15	11.47 ( $\pm 0.01$ )	701.61 ( $\pm 0.27$ )
313.15	11.73 ( $\pm 0.01$ )	689.83 ( $\pm 0.30$ )

TABLE IV. The standard partial molar enthalpy of activation for viscous flow of a solvent–solvent mixtures,  $\Delta H_1^{\ominus*}$ , and its deviation from the standard partial molar enthalpy of activation for viscous flow of the solute,  $\Delta H_2^{\ominus*}$ ,  $(\Delta H_2^{\ominus*} - \Delta H_1^{\ominus*})$ , along with the standard partial molar entropy of activation for viscous flow of a solvent–solvent mixture,  $\Delta S_1^{\ominus*}$ , and its deviation from the standard partial molar entropy of activation for viscous flow of the solute,  $\Delta S_2^{\ominus*}$ ,  $(\Delta S_2^{\ominus*} - \Delta S_1^{\ominus*})$ , for Fe<sup>III</sup>(salen)Cl in different aqueous methanol solutions;  $w_1$  – mass fraction of methanol

$w_1$	$\Delta H_1^{\ominus*}$ $\text{kJ mol}^{-1}$	$(\Delta H_2^{\ominus*} - \Delta H_1^{\ominus*})$ $\text{kJ mol}^{-1}$	$\Delta S_1^{\ominus*}$ $\text{J mol}^{-1}\text{K}^{-1}$	$(\Delta S_2^{\ominus*} - \Delta S_1^{\ominus*})$ $\text{J mol}^{-1}\text{K}^{-1}$
1.00	9.28 ( $\pm 0.01$ )	587.17 ( $\pm 7.34$ )	-2.31 ( $\pm 0.04$ )	214.20 ( $\pm 4.09$ )
0.90	8.56 ( $\pm 0.02$ )	988.83 ( $\pm 7.72$ )	-6.54 ( $\pm 0.07$ )	1617.19 ( $\pm 6.17$ )
0.80	5.62 ( $\pm 0.01$ )	1307.11 ( $\pm 4.45$ )	-17.89 ( $\pm 0.03$ )	2423.24 ( $\pm 8.32$ )
0.70	4.95 ( $\pm 0.01$ )	1592.97 ( $\pm 3.39$ )	-20.72 ( $\pm 0.03$ )	3135.12 ( $\pm 6.59$ )
0.60	3.37 ( $\pm 0.01$ )	1552.35 ( $\pm 4.52$ )	-26.70 ( $\pm 0.02$ )	2767.67 ( $\pm 7.28$ )

Table III shows that the  $\Delta\mu_1^{\ominus*}$  values are almost invariant of the solvent composition and temperature, implying that  $\Delta\mu_2^{\ominus*}$  is dependent mainly on the viscosity  $B$ -coefficients and the  $(\phi_{V,2}^0 - \phi_{V,1}^0)$  terms. The values  $\Delta\mu_2^{\ominus*}$  contain the change in the free energy of activation of solute molecules in presence of

solvent as well as the contribution from the movement of solute molecules. The  $\Delta\mu_2^{\ominus*}$  values were positive at all the experimental temperatures and decreased as the temperature increased and increased as the content of water in the ternary solutions (except for those with  $w_1 = 0.90$ ) increased. Such a trend of the  $\Delta\mu_2^{\ominus*}$  values suggest that the viscous flow becomes easier at higher temperatures but becomes more difficult with increased amount of water in the ternary solutions, *i.e.*, the formation of the transition state becomes less favourable with increased amounts of water but higher temperature favour its formation.<sup>45</sup>

According to Feakins *et al.*,<sup>47</sup> a solute molecule interacts with every solvent molecule and the sum of these interactions for all solute and solvent molecules is collectively defined as the solute–solvent interaction. A solute molecule interacts with all the solvent molecules in solution including any solvent molecule in its transition state. Thus the effect of the solute on the activation free energy of the solvent molecule is the difference between the solvation energies of the solute in the ground state solvent and the transition state solvent or free energy of transfer,  $\Delta G_2^{\ominus*}(1 \rightarrow 1')$  between them. The second contribution to  $\Delta\mu_2^{\ominus*}$  comes from the movement of the solute through its own viscous transition state,  $\Delta G_2^{\ominus*}(2 \rightarrow 2')$ . Hence, the term  $\Delta\mu_2^{\ominus*}$  can also expressed as:

$$\Delta\mu_2^{\ominus*} = \Delta G_2^{\ominus*}(1 \rightarrow 1') + \Delta G_2^{\ominus*}(2 \rightarrow 2') \quad (10)$$

The values of  $\Delta G_2^{\ominus*}(2 \rightarrow 2')$  can be approximated with the  $\Delta\mu_1^{\ominus*}$  values and the values of  $\Delta G_2^{\ominus*}(1 \rightarrow 1')$  simply become equal to the  $(\Delta\mu_2^{\ominus*} - \Delta\mu_1^{\ominus*})$  values.

Thus, the quantity  $(\Delta\mu_2^{\ominus*} - \Delta\mu_1^{\ominus*})$  is the change in the activation energy per mole of solute on replacing one mole of solvent by one mole of solute at infinite dilution. The obtained values of  $(\Delta\mu_2^{\ominus*} - \Delta\mu_1^{\ominus*})$  are positive for all the solvent mixtures and the values decrease almost linearly as the temperature increases for all the solvent mixtures, but they increase with further addition of water in the ternary solutions (except for those with  $w_1 = 0.90$ ). The positive  $(\Delta\mu_2^{\ominus*} - \Delta\mu_1^{\ominus*})$  values and their negative temperature dependence with a similar trend in the viscosity *B*-coefficients for  $\text{Fe}^{\text{III}}(\text{salen})\text{Cl}$  indicated the structure making ability of the solute and transfer of solute molecules from the ground state solvent to the transition state solvent is thermodynamically hindered.

Table IV shows that the  $\Delta H_2^{\ominus*}$  values are positive for all the solvent systems and thus indicate rupture and distortion of the solvation bonds or intermolecular forces in the activated state of viscous flow and that the viscous process is endothermic. Thus, the viscous flow will be accompanied by a decrease in order and thus positive  $\Delta S_2^{\ominus*}$  values were obtained for all the studied solutions. However, the negative  $\Delta S_1^{\ominus*}$  values for all the solvent mixtures may be attributed to the negative entropy of mixing of the solutions over the entire range of concentration for aqueous methanol; such a negative entropy of mixing originates from the strong association between the solvent molecules at low methanol contents<sup>35</sup>

and the tendency of the solvent molecules to segregate and form clusters<sup>48-50</sup> in aqueous methanol solutions, which dominate the thermodynamics of aqueous methanol solutions.<sup>51,52</sup>

### CONCLUSIONS

In the present study, derived parameters such as partial molar volumes ( $\phi_V^0$ ), partial molar expansibilities ( $\phi_E^0$ ), viscosity *B*-coefficients and various activation parameters for viscous flow for the under investigation Fe<sup>III</sup>(salen)Cl indicate the presence of strong solute–solvent interactions and these interactions are further strengthened at higher content of water in the ternaries but decrease at higher temperatures. The results further show that Fe<sup>III</sup>(salen)Cl is preferentially more solvated by water than methanol and it acts as a net structure promoter in the studied ternary solutions. The UV–Vis absorption spectra of the ternary solutions support of the obtained results. A transition state theory treatment of viscosity *B*-coefficients revealed that the transfer of the solute molecules from ground state solvent to transition state solvent is thermodynamically hindered and the viscous process is endothermic.

### SUPPLEMENTARY MATERIAL

The physical properties of different aqueous methanol solutions and experimental densities, viscosities of Fe<sup>III</sup>(salen)Cl solutions along with derived parameters at the experimental temperatures and their dependence on solvent composition and temperatures, *etc.* (listed in Tables S-I–S-III and Figs. S-1–S-4) are available electronically from <http://www.shd.org.rs/JSCS/> or from the authors on request.

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### ИЗВОД

ПОНАШАЊЕ РАСТВОРА КОЈИ САДРЖИ (N,N'-БИС(САЛИЦИЛИДЕН)-  
ЕТИЛЕНДИАМИНАТО)ГВОЖЂЕ(III)-ХЛОРИД У СМЕШИ ВОДЕ И МЕТАНОЛА  
НА 298,15; 303,15 И 313,15 К

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У овом раду су одређене парцијалне моларне запремине ( $\phi_V^0$ ) и *B*-коэффицијенти Jones–Dole једначине (N,N'-бис(салицилиден)етилендиаминато)гвожђе(III)-хлорида, скраћено Fe<sup>III</sup>(salen)Cl, у растворима смеше растварача воде и метанола мерењем густине и вискозности раствора на температурама 298,15; 303,15 и 313,15 К под атмосферским притиском. Привидне моларне запремине ( $\phi_V$ ) и густине ( $\rho$ ) су коришћене за прорачун промена привидних моларних запремина од температуре ( $\phi_E$ ) и парцијалних моларних запремина од температуре ( $\phi_E^0$ ) као и одређивање облика температурне зависности при константном притиску ( $\partial\phi_E^0/\partial T$ )<sub>p</sub> у растворима Fe<sup>III</sup>(salen)Cl са циљем да се

открије природа различитих интеракција у тернарним растворима . Теорија прелазног стања је примењена у анализи *B* коефицијената на основу активационих параметара вискозног тока. Свеукупни резултати указују на јаке интеракције растворак–растварач између Fe<sup>III</sup>(salen)Cl и молекула растварача, превасходно молекула воде као и да се Fe<sup>III</sup>(salen)Cl понаша као компонента која стабилизује структуру тернарних раствора. UV-Vis апсорпциони спектри тернарних раствора потврђују добијене резултате.

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