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## Conductometric measurements of complexation study between 4-Isopropylcalix[4]arene and Cr<sup>3+</sup> cation in THF–DMSO binary solvents

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### ABSTRACT

In the present work, the conductometric measurements for complexation process between Cr<sup>3+</sup> cation and the macrocyclic ionophore, 4-Isopropylcalix[4]arene (IPC4) were studied in tetrahydrofuran–dimethylsulfoxide (THF–DMSO) binary non-aqueous medium at different temperatures. The results reveal that the stoichiometry of the IPC4–Cr<sup>3+</sup> complex in all binary mixed solvents is 1:1. A non-linear behavior was observed for changes of log *K<sub>f</sub>* of this complex versus the composition of the binary mixed solvents, which was explained on the basis of changes occurring in the structure of the mixed solvents and also the preferential solvation of the cation, ionophore and the resulting complex in the solution. The thermodynamic parameters ( $\Delta H^{\circ}_c$  and  $\Delta S^{\circ}_c$ ) for the formation of IPC4–Cr<sup>3+</sup> complexes were obtained from the temperature dependence of the stability constant using the van't Hoff plots. The results obtained in this study, show that the formed complex is enthalpy destabilized, but entropy stabilized and the values of the mentioned parameters are affected strongly by the nature and composition of the binary mixed solvents. The experimental data was tested by using artificial neural network (ANN) program and was in a good agreement with the estimated data.

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### 1. Introduction

Calixarenes as a new generation of macrocyclic compounds with pre-organized and semi-rigid molecular structure as well as three dimensional nature of the complexation cavity, exhibit high selectivity with enhanced complexation properties toward target ions. Therefore, they can be used as ideal ionophores with high selectivity

in the fabrication of novel ISEs with superior low detection limit and wide dynamic range [1–6]. The selectivity of ionophore can be explained in terms of the thermodynamic stability, which is a complicated combination of enthalpy and entropy of forming complex. The higher stability of complexes implies more selective interactions that occur between macrocyclic compounds and metal ions [7–14].

The conductometric measurements have been commonly used for complexes reactions studies between the macrocyclic ligands and various species of ions in different solvents due to such advantages of inexpensive cost, instrumental easy used, accurate and sensitive measurements and a simple experimental arrangement [15–18].

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Other physicochemical techniques like potentiometry [19–24], NMR spectrometry [25], spectrophotometry [26–28], calorimetry [29] and polarography [30] have been reported besides the conductometry method for the investigation of complexation process. Such studies can initiate a new horizon to investigate the effect of solvents and their mixtures in the development of pharmaceutical systems or a way to cross the blood organ barrier [31,32].

The selectivity of macrocyclic ligands toward the target cations and the stability of formed complexes is followed by several factors such as the density of charges and polarizability of metal cations, the number of donor atoms and the nature of substituents in the macrocyclic compounds, the properties of co-anion with the cations and the cavity size of macrocyclic ligand [33–35]. Moreover, the type of solvent which is used in complexation reactions influences the stability and even in some cases, the stoichiometry of the formed complexes [36].

Numerous studies on complexation reaction between the macrocyclic ligands and metal cations in different non-aqueous solvents have been reported until now, but the characteristic studies of complex formation based on non-aqueous mediums were far fewer [37–39]. In fact, non-aqueous mediums have enormous applications in a wide range of pure and applied chemistry [40–44]. Hence, this study makes a great effort to investigate the influence of solvent properties on the thermodynamic parameters of complex formation between 4-Isopropylcalix[4]arene with chromium (III) ion in tetrahydrofuran–dimethylsulfoxide (THF–DMSO) binary mixtures based on the conductometric method at different temperatures. To our certain knowledge, heretofore, there have been no reports of the thermodynamic study between IPC4 with any metal cations.

## 2. Experimental

### 2.1. Materials

The novel ionophore namely 4-Isopropylcalix[4]arene from Aldrich and chromium (III) nitrate from Merck were purchased and used as received and dried in a vacuum desiccator over P<sub>2</sub>O<sub>5</sub>. Tetrahydrofuran (THF) and dimethylsulfoxide (DMSO) (all from the Merck) were used as received with the highest purity.

### 2.2. Apparatus and procedure

Conductance measurements were carried out with a digital Cyberscan conductivity/TDS/°C/°F meter (model 510 CON). The conductivity/TDS electrode with a cell constant of 1.0 cm<sup>-1</sup> made of stainless steel rings was used throughout the studies. In all measurements, a thermostated water-bath was applied for thermostating the cell at the desired temperatures within ± 0.01 °C.

The experimental procedure was prepared according to previous literatures [15]. The formation constant of the complexes will be obtained by using the procedure designated as follows. A solution of metal ion with the concentration of 5.0 × 10<sup>-4</sup> M was prepared and fixed in a titration cell. After that, the ligand with concentration of 2.5 × 10<sup>-2</sup> M was added to the titration cell using a

micropipette. During the reaction, the desired temperature was fixed and a magnetic stirrer has been used to form a homogenized condition in a titration cell. The conductivity values were measured before and after each titration of the ligand's solution. The procedure was repeated for all formed complexes between the IPC4 and Cr(III) cations in THF–DMSO binary system (mol% THF; 0.00%, 9.99%, 22.66%, 39.73%, 63.72% and 100.00%) at different temperature (15, 25, 35 and 45 °C).

### 2.3. Complex Formation Constant (K<sub>f</sub>)

The formation constant of resulted 1:1 complex between IPC4 compound and Cr(III) metal cation can be expressed in the following equilibrium [45]:



where S is the solvent molecule, and x, y and z are the solvation numbers of the Cr(III) cation, the IPC4 ligand, and the resulting complex, respectively. According to the equilibrium 1, the complex formation process affected by various factors such as the nature of metal cation, macrocyclic compound and solvent molecules. Solvation of the metal cation (Cr<sup>3+</sup>) and ligand (IPC4) by the solvent molecules can be resulted to enhance or reduce the resulted 1:1 complex formation constant. The complex reaction of IPC4 ligand with Cr<sup>3+</sup> cations lead to reduce the number of free metal cations in the solution. Due to the different mobility of free cations and their complexes, the conductivity of the solution will be changed [46]. Then, the conductometric method can be applied for the investigation of complex reaction of IPC4 ligand with Cr<sup>3+</sup> cation in this study. The equilibrium 2 can be expressed for the 1:1 complexation of Cr<sup>3+</sup> cation with IPC4 ligand [47]:



The corresponding equilibrium constant, K<sub>f</sub>, is expressed as:

$$K_f = \frac{[\text{Cr-IPC4}^{3+}] \cdot f_{(\text{Cr-IPC4})^{3+}}}{[\text{Cr}^{3+}] [\text{IPC4}] \cdot f_{(\text{Cr}^{3+})} \cdot f_{(\text{IPC4})}} \quad (3)$$

In this equation, [Cr–IPC4<sup>3+</sup>], [Cr<sup>3+</sup>] and [IPC4] represent the molar concentration of the resulted 1:1 complex, free Cr(III) cation and free IPC4 macrocyclic ligand, respectively. *f* denotes the activity coefficients of the species in the electrolyte solution. Since the highly dilute condition was used in this work, the activity coefficient of macrocyclic compound, *f*<sub>(IPC4)</sub>, the free metal ions, *f*<sub>(Cr<sup>3+</sup>)</sub> and complex, *f*(Cr–IPC<sup>3+</sup>), reasonably assumed to be unity. Dilute condition is where the ionic strength is less than 0.001 M. According to the Debye–Hückel limiting law of electrolytes leads to the conclusion that *f*<sub>(Cr–IPC<sup>3+</sup>)</sub> ≈ *f*<sub>(Cr<sup>3+</sup>)</sub> [48]. Thus, the above equation can be simplified as illustrated below:

$$K_f = \frac{[\text{Cr-IPC4}^{3+}]}{[\text{Cr}^{3+}] [\text{IPC4}]} \quad (4)$$

The specific conductivity (*k*) of each ionic species in the titration reaction can be expressed by the following equation which is presented by K<sub>(Cr<sup>3+</sup>)</sub> and K<sub>(Cr–IPC<sup>3+</sup>)</sub> the conductivity of cationic salt and 1:1 resulted complex, respectively:

$$K = K_{(\text{Cr}(\text{NO}_3)_3)} + K_{((\text{Cr}-\text{IPC4})^{3+}, 3\text{NO}_3^-)} \quad (5)$$

The following equations show the molar conductance of chromium (III) salt before the addition of IPC4 macrocyclic compound and molar conductance of  $(\text{Cr}-\text{IPC4})^{3+}$  complex salt:

$$\Lambda_{(\text{Cr}(\text{NO}_3)_3)} = \frac{k_{(\text{Cr}(\text{NO}_3)_3)}}{[\text{Cr}^{3+}]} \quad (6)$$

$$\Lambda_{((\text{Cr}-\text{IPC4})^{3+}, 3\text{NO}_3^-)} = \frac{k_{((\text{Cr}-\text{IPC4})^{3+}, 3\text{NO}_3^-)}}{[(\text{Cr}-\text{IPC4})^{3+}]} \quad (7)$$

$$[\text{IPC4}] = \frac{-(1 + K_f[\text{Cr}^{3+}]_t - K_f[\text{IPC4}]_t) \pm \sqrt{(1 + K_f[\text{Cr}^{3+}]_t - K_f[\text{IPC4}]_t)^2 + 4K_f[\text{IPC4}]_t^{1/2}}}{2K_f} \quad (18)$$

The total concentration of the chromium (III) cation which is the combination of the concentration of free and complexed form can be illustrated as:

$$[\text{Cr}^{3+}]_t = [\text{Cr}^{3+}] + [(\text{Cr}-\text{IPC4})^{3+}] \quad (8)$$

$\Lambda_{obs}$  will be obtained as the molar conductance of the solution during titration by the following equation:

$$\Lambda_{obs} = \frac{k}{[\text{Cr}^{3+}]_t} \quad (9)$$

The final equations will be resulted by combining and simplifying the obtained equations as stated below:

$$\Lambda_{obs}[\text{Cr}^{3+}]_t = \Lambda_{(\text{Cr}(\text{NO}_3)_3)}[\text{Cr}^{3+}] + \Lambda_{((\text{Cr}-\text{IPC4})^{3+}, 3\text{NO}_3^-)}[(\text{Cr}-\text{IPC4})^{3+}] \quad (10)$$

$$\begin{aligned} [\text{Cr}^{3+}]_t &= [\text{Cr}^{3+}] + K_f[\text{Cr}^{3+}][\text{IPC4}] \\ &= [\text{Cr}^{3+}](1 + K_f[\text{IPC4}]) \end{aligned} \quad (11)$$

On the other hand,  $[\text{IPC4}]_t$  as the total concentration of ligand can be described as follow:

$$[\text{IPC4}]_t = [(\text{Cr}-\text{IPC4})^{3+}] + [\text{IPC4}] \quad (12)$$

And, as like as Eq. (11), the following equation will be obtained:

$$[\text{IPC4}]_t = [\text{IPC4}] + K_f[\text{Cr}^{3+}][\text{IPC4}] \quad (13)$$

The equation below is obtained by substituting Eq. (4) into Eq. (10):

$$\Lambda_{obs}[\text{Cr}^{3+}]_t = \Lambda_{(\text{Cr}(\text{NO}_3)_3)}[\text{Cr}^{3+}] + \Lambda_{((\text{Cr}-\text{IPC4})^{3+}, 3\text{NO}_3^-)}K_f[\text{Cr}^{3+}][\text{IPC4}] \quad (14)$$

And then, simplify by substituting Eq. (11) into Eq. (14):

$$\begin{aligned} \Lambda_{obs} &= \frac{[\text{Cr}^{3+}]\Lambda_{(\text{Cr}(\text{NO}_3)_3)} + K_f\Lambda_{((\text{Cr}-\text{IPC4})^{3+}, 3\text{NO}_3^-)}[\text{Cr}^{3+}][\text{IPC4}]}{[\text{Cr}^{3+}](1 + K_f[\text{IPC4}])} \\ &= \frac{\Lambda_{(\text{Cr}(\text{NO}_3)_3)} + K_f\Lambda_{((\text{Cr}-\text{IPC4})^{3+}, 3\text{NO}_3^-)}[\text{IPC4}]}{(1 + K_f[\text{IPC4}])} \end{aligned} \quad (15)$$

The combination of Eqs. (11) and (13) will result the Eq. (16) as below:

$$[\text{IPC4}]_t = [\text{IPC4}] + \frac{K_f[\text{Cr}^{3+}]_t}{1 + K_f[\text{IPC4}]} \quad (16)$$

Rearranging Eq. (16) yields:

$$K_f[\text{IPC4}]^2 + (1 + K_f[\text{Cr}^{3+}]_t - K_f[\text{IPC4}]_t)[\text{IPC4}] - [\text{IPC4}]_t = 0 \quad (17)$$

The molar concentration of IPC4 ligand can be found by solving the Eq. (17) as follow:

The molar concentration of IPC4 ligand during the titration reaction is achieved by solving the Eq. (17) (the amount of positive root) and by substituting this obtained amount into the Eq. (15), the values of molar conductance of metal calixarene salt and complex formation constant can be attained.

In knowing the values of total concentrations of chromium (III) cation and IPC4 ligand and the molar conductance of uncomplex of chromium (III) nitrate, the  $[\text{IPC4}]$  value will be resulted in the Eq. (17). By substituting all estimated values in Eq. (15), the amount of calculating molar conductance ( $\Lambda_{cal}$ ) can be obtained which is followed by achieving the best value of complex formation constant ( $K_f$ ) based on the comparison of the value of calculated molar conductance ( $\Lambda_{cal}$ ) and observed molar conductance ( $\Lambda_{obs}$ ).

#### 2.4. GENPLOT program

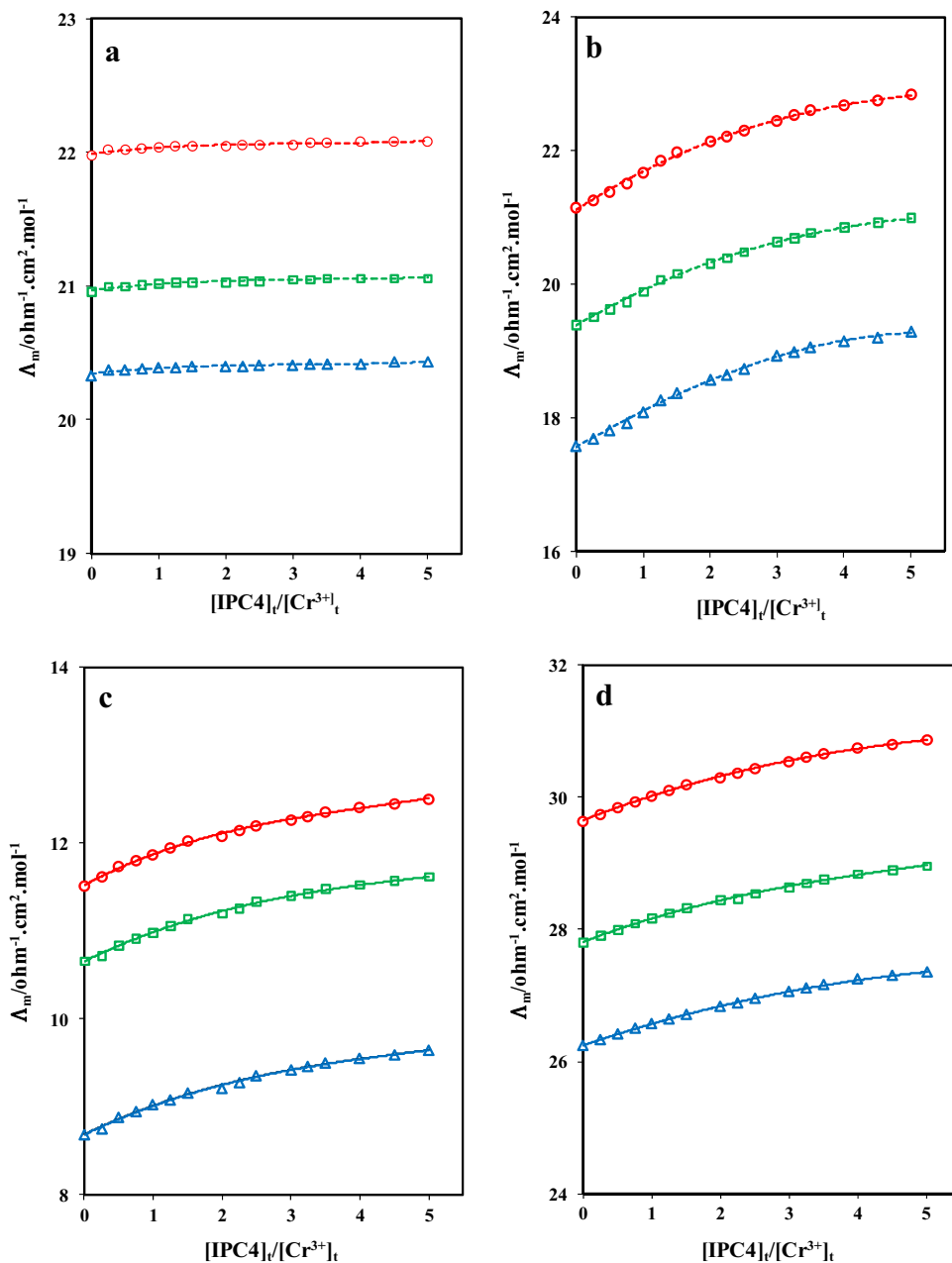
The GENPLOT computer program as the nonlinear least-squares program was used in this study to obtain the best value of complex formation constant for the titration reaction between the IPC4 ligand and  $\text{Cr}^{3+}$  cation in DMSO and THF solvent and their media [49]. This program finds the minimum difference in value between the calculated and observed values of molar conductance as a function of  $[\text{IPC4}]/[\text{Cr}^{3+}]$  molar ratios by fitting the data into the function based on Eqs. (15) and (16). The function includes four parameters,  $\Lambda_{(\text{Cr}(\text{NO}_3)_3)}$ ,  $\Lambda_{((\text{Cr}-\text{IPC4})^{3+}, 3\text{NO}_3^-)}$ ,  $K_f$  and  $[\text{Cr}^{3+}]_t$  as the variable and non-variable parameters, respectively.

#### 2.5. Enthalpy and entropy of complexation process

The values of standard enthalpy ( $\Delta H^\circ_c$ ), standard entropy ( $\Delta S^\circ_c$ ) and standard Gibbs free energy ( $\Delta G^\circ_c$ ) for the complexation reaction of IPC4 with  $\text{Cr}^{3+}$  were calculated from the thermodynamic relation Eqs. (19) and (20) [50].

$$\Delta G^\circ_c = -RT \ln K_f \quad (19)$$

$$\Delta G^\circ_c = \Delta H^\circ_c - T\Delta S^\circ_c \quad (20)$$



**Fig. 1.** Molar conductance vers. mole ratio plots for (IPC4–Cr)<sup>3+</sup> complexes in (a) pure THF (b) pure DMSO (c) mol% DMSO = 43.3 and (d) mol% DMSO = 82.1 at different temperatures ( $\Delta$  = 25 °C,  $\square$  = 35 °C,  $\circ$  = 45).

where  $R$  and  $T$  are known as the universal gas constant and absolute temperature, respectively. The value of standard enthalpy ( $\Delta H_c^\circ$ ) for the complexation reaction was obtained by plotting the graph of  $\ln K_f$  versus  $1/T$  (Van't Hoff plot), in different temperatures as follows:

$$\ln K_f = \frac{-\Delta H_c^\circ}{RT} + \frac{\Delta S_c^\circ}{R} \quad (21)$$

$$\Delta H_c^\circ = -R \times \text{Slope} \quad (22)$$

### 3. Results and discussions

#### 3.1. Stoichiometry of the complex

Many researchers were reported to investigate the effect of nature and composition of non-aqueous solutions which impressively affect the stability, thermodynamic, stoichiometry and selectivity of complexation of macrocyclic compounds with metal cations [51–54]. In this

study, the changes of molar conductance ( $\Lambda_m$ ) of the solution versus the molar ratio of IPC4 ligand to chromium (III) cation ( $[\text{IPC4}]/[\text{Cr}^{3+}]$ ) for the complexation titration in pure THF, pure DMSO and their binary mixtures (mol%) were studied at different temperatures (25, 35 and 45 °C). The resulting of four plots of  $\Lambda_m$  values as a function of ( $[\text{IPC4}]/[\text{Cr}^{3+}]$ ) molar ratios in pure THF, DMSO, THF–DMSO (mol% DMSO = 43.3) and (mol% DMSO = 82.1) media are presented in Fig. 1. As can be seen in Fig. 1(A), the  $\Lambda_m$  versus ( $[\text{IPC4}]/[\text{Cr}^{3+}]$ ) plots are not sharp and show a gradual increase in  $\Lambda_m$  parallel to the increase of the IPC4 ligand concentration. This corresponds to the forming (IPC4–Cr<sup>3+</sup>) complex which is more mobile than free solvated Cr<sup>3+</sup> cation. It seems that in all cases, the addition of IPC4 ligand to the chromium (III) cation solution results in the formation of 1:1 [Cr<sup>3+</sup>:IPC4] complex.

As it is clear from Table 1, the addition of IPC4 ligand to Cr<sup>3+</sup> cation in all solvent systems at different temperatures shows an increment in molar conductivity by increasing the ligand concentration. This indicates that the (IPC4–Cr<sup>3+</sup>) complex is more mobile than free solvated Cr<sup>3+</sup> cation.

### 3.2. Stability constant of the complex

The formation constant values ( $\log K_f$ ) of all formed complexes in different mol ratio of binary solvents and temperatures were obtained by using GENPLOT computer program and are summarized in Table 2. The results show that the stability constants ( $\log K_f$ ) for (IPC4–Cr<sup>3+</sup>) complexes increased by the increasing in temperature from 25 °C to 45 °C in most of the solvent systems. This is an indication for an endothermic complexation reaction between IPC4 ligand and Chromium (III) cation [1]. The similar behaviors were observed for all complexes and the results indicated that stronger complexes were formed at higher temperatures.

The ion-pair formation constant for (IPC4–Cr<sup>3+</sup>) in the solvent with the known amount of dielectric constant ( $D$ ) can be expressed as the following equation [2]:

$$K_{\text{ion-pair}} = \frac{A}{D} \cdot \frac{Z_+ Z_-}{r^2} \quad (23)$$

where  $Z_+$  and  $Z_-$  represent the charge of the complex ions, counter anion, and  $r$  as the constant distance between the centers of the ions.

In this study, with the assumption that the large amount of ionic size of cations and anions (Cr<sup>3+</sup> and NO<sub>3</sub><sup>-</sup>) and relatively high amount of dielectric constant for applied DMSO solvent ( $\epsilon = 47$ ), in addition with an extremely low concentration of used ions, the ion pair association is negligible and consequently, the phenomenon of ionic association was not included in current work [16].

As it is obvious from Table 2, with the increasing of the concentration of DMSO with higher Gutmann donor number of 29.8 in compression with THF with lower Gutmann donor number of 20.0, the chromium (III) cation was strongly solvated by the molecular solvents and hardly can be complexed by the IPC4 ligand [3–5].

As it is mentioned earlier, solvent properties can be considered as one of the most important parameters that affects the formation constant of ligand-cation complex.

**Table 1**  
Molar conductivity of 4-isopropylcalix[4]arene–Cr(NO<sub>3</sub>)<sub>3</sub> system in THF–DMSO binary mixed solvent at different temperatures.

$\frac{[\text{IPC4}]}{[\text{Cr}^{3+}]}$	$\Lambda_m$ (ohm <sup>-1</sup> cm <sup>2</sup> mol <sup>-1</sup> )																	
	Pure THF			77.8% THF			56.7% THF			36.8% THF			17.9% THF			Pure DMSO		
	25 °C	35 °C	45 °C	25 °C	35 °C	45 °C	25 °C	35 °C	45 °C	25 °C	35 °C	45 °C	25 °C	35 °C	45 °C	25 °C	35 °C	45 °C
0	20.33	20.96	21.98	15.19	17.31	19.36	8.68	10.66	11.51	19.72	22.81	26.38	26.24	27.81	29.64	17.58	19.39	21.14
0.25	20.37	21.00	22.02	15.22	17.35	19.40	8.75	10.72	11.61	19.82	22.95	26.49	26.33	27.91	29.74	17.69	19.51	21.26
0.5	20.37	21.00	22.02	15.22	17.35	19.41	8.88	10.84	11.73	19.92	23.08	26.60	26.42	28.00	29.84	17.80	19.63	21.38
0.75	20.38	21.01	22.03	15.23	17.36	19.41	8.95	10.92	11.80	20.04	23.19	26.72	26.50	28.09	29.93	17.92	19.74	21.50
1	20.39	21.02	22.04	15.24	17.36	19.41	9.02	10.98	11.86	20.08	23.27	26.79	26.58	28.17	30.02	18.08	19.89	21.67
1.25	20.39	21.03	22.05	15.24	17.37	19.42	9.08	11.06	11.94	20.36	23.50	27.06	26.65	28.25	30.10	18.25	20.07	21.84
1.5	20.40	21.03	22.05	15.25	17.37	19.42	9.16	11.14	12.03	20.48	23.61	27.19	26.72	28.33	30.18	18.37	20.16	21.98
2	20.40	21.03	22.05	15.25	17.37	19.42	9.21	11.20	12.08	20.66	23.80	27.35	26.83	28.45	30.30	18.56	20.31	22.14
2.25	20.40	21.04	22.06	15.25	17.38	19.43	9.27	11.26	12.14	20.72	23.85	27.40	26.89	28.47	30.37	18.63	20.39	22.20
2.5	20.41	21.05	22.06	15.26	17.39	19.44	9.35	11.34	12.20	20.82	23.94	27.49	26.96	28.54	30.44	18.73	20.48	22.29
3	20.41	21.05	22.06	15.26	17.39	19.44	9.42	11.40	12.26	21.04	24.16	27.65	27.06	28.64	30.54	18.92	20.63	22.44
3.25	20.42	21.05	22.07	15.27	17.40	19.44	9.46	11.43	12.30	21.06	24.20	27.74	27.11	28.70	30.60	18.98	20.69	22.53
3.5	20.42	21.06	22.07	15.27	17.40	19.45	9.50	11.48	12.35	21.14	24.29	27.81	27.17	28.76	30.66	19.06	20.77	22.60
4	20.42	21.06	22.08	15.28	17.41	19.45	9.55	11.53	12.41	21.22	24.37	27.90	27.25	28.84	30.74	19.14	20.85	22.68
4.5	20.43	21.06	22.08	15.28	17.41	19.46	9.59	11.57	12.45	21.28	24.43	27.95	27.30	28.90	30.80	19.20	20.92	22.74
5	20.43	21.06	22.08	15.28	17.41	19.46	9.64	11.62	12.50	21.36	24.51	28.03	27.36	28.96	30.86	19.28	20.99	22.83

The competition between solvent and ionophore molecules in binding to  $\text{Cr}^{3+}$  cations and solvation of ligand by solvent molecules may influence upon complex formation between IPC4 ligand and  $\text{Cr}^{3+}$  cation in the binary mixed solutions.

The changes in stability constant ( $\log K_f$ ) of the formed complex versus the composition of the THF–DMSO media at different temperatures are not linear as shown in Fig. 2. This pattern is probably due to solvent–solvent interaction that changed the structure of the solvent mixtures and consequently changed the solvation properties of the chromium (III) cations, IPC4 ligand and the resulting complexes [55]. Moreover, some parameters such as preferential solvation of metal cations, macrocyclic ligand, the changing characteristics of binary solvents mixtures and different temperatures can result in the different complexation process.

### 3.3. Thermodynamic Parameters ( $\Delta G^\circ_c$ , $\Delta H^\circ_c$ , $\Delta S^\circ_c$ ) of the complex

The graphs of  $\ln K_f$  versus  $1/T$  were plotted for all mol percentage of SMSO solvent. The standard enthalpy ( $\Delta H^\circ_c$ ) and standard entropy ( $\Delta S^\circ_c$ ) parameters were determined according to the slope of van't Hoff plots (Fig. 3) and the relationship of  $\Delta G^\circ_{c,298.15} = \Delta H^\circ_c - 298.15 \Delta S^\circ_{c,298.15}$  respectively. The calculated results are illustrated in Table 3. The enthalpy and entropy values of  $(\text{IPC4-Cr})^{3+}$  complexes change with different factors such as variation of flexibility of macrocyclic ligand during the complexation process, the amounts of IPC4–solvent,  $\text{Cr}^{3+}$ –solvent,  $(\text{IPC4-Cr})^{3+}$ –solvent and even solvent–solvent interaction [20]. Therefore, it can be concluded that, these thermodynamic parameters varied with the composition and nature of applied binary solvents as can be seen from Table 3.

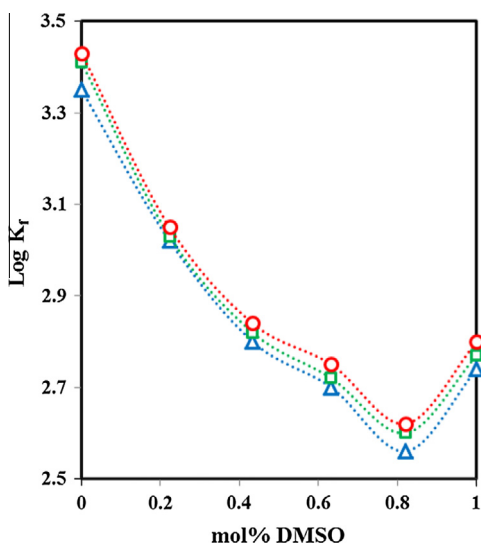


Fig. 2. Changes of the stability constant ( $\log K_f$ ) of  $(\text{IPC4-Cr})^{3+}$  complexes with the composition of DMSO–THF binary systems at different temperatures ( $\Delta = 25^\circ\text{C}$ ,  $\square = 35^\circ\text{C}$ ,  $\circ = 45^\circ\text{C}$ ).

Table 2

$\log K_f$  values of  $(\text{IPC4-Cr})^{3+}$  complex in THF–DMSO binary mixed solvents at different temperatures.

Complex Solvent medium <sup>b</sup>	$\log K_f \pm \text{SD}^a$		
	25 °C	35 °C	45 °C
Pure THF	$3.35 \pm 0.16$	$3.41 \pm 0.14$	$3.43 \pm 0.16$
22.2% DMSO–77.8% THF	$3.02 \pm 0.18$	$3.03 \pm 0.22$	$3.05 \pm 0.19$
43.3% DMSO–56.7% THF	$2.80 \pm 0.06$	$2.82 \pm 0.04$	$2.84 \pm 0.05$
63.2% DMSO–36.8% THF	$2.70 \pm 0.11$	$2.72 \pm 0.07$	$2.75 \pm 0.09$
82.1% DMSO–17.9% THF	$2.56 \pm 0.03$	$2.60 \pm 0.04$	$2.62 \pm 0.03$
Pure DMSO	$2.74 \pm 0.07$	$2.77 \pm 0.05$	$2.80 \pm 0.06$

<sup>a</sup> SD = Standard deviation.

<sup>b</sup> Composition of binary mixture is expressed in mol% for solvent system.

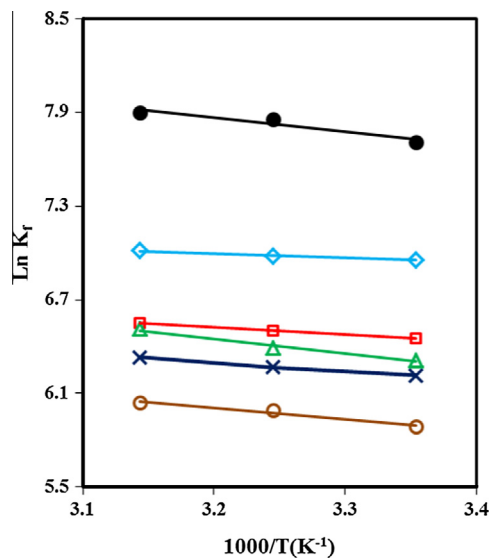


Fig. 3. Van't Hoff plots for  $(\text{IPC4-Cr})^{3+}$  complexes in DMSO–THF binary systems (mol% DMSO:  $\Delta = 100$ ,  $\circ = 82.1$ ,  $\times = 63.2$ ,  $\square = 43.3$ ,  $\diamond = 22.2$ ,  $\bullet = 0$ ).

According to the obtained data, in most cases the changes in  $\Delta H^\circ_c$  for the  $(\text{IPC4-Cr})^{3+}$  formed complexes are negligible, whereas the changes in  $\Delta S^\circ_c$  are significant. Therefore, the formation of complexes between IPC4 ligand and  $\text{Cr}^{3+}$  cation in THF–DMSO mixtures are entropy stabilized but enthalpy destabilized. The different solvent–solvent interactions in all solvent systems and the changes in the flexibility of ligand during complexation contribute to the change in entropy. Additionally, deformation of the macrocyclic ligand and intermolecular ligand–ligand repulsions resulted in the change of ligand enthalpy in the forming of complex reaction. The increase in degree of freedom which is caused by desolvation of cation might result in some positive entropic gain, as well as releasing the solvent molecules that involved in the interaction with ionophore. As it is demonstrated in Table 3, there is no change monotonically of the thermodynamic values,  $\Delta H^\circ_c$  and  $\Delta S^\circ_c$ , with the composition of applied solvents. As it is stated, there are many factors which contribute to the changes of enthalpy and entropy, therefore no regularities are expected between them and the solvent composition. Moreover, literature surveys showed that a non-monotonic

behavior is observed for thermodynamic functions of several macrocyclic compound-metal ion complex formations in some binary mixed solvents [22,23].

The calculated value of  $\Delta G^\circ_c$  in all cases shows negative values. This is an evidence of the ability of the IPC4 ligand to form stable complexes with  $\text{Cr}^{3+}$  cations and the process were spontaneous [30]. It is clear that the observed increase or decrease in  $\Delta H^\circ_c$  value which depends on the nature of the metal ion will be compensated by an increase (or decrease) in the corresponding  $\Delta S^\circ_c$  value. Then the small changes of  $\Delta G^\circ_c$  values will be resulted due to this compensating effect for  $\Delta H^\circ_c$  and  $\Delta S^\circ_c$ , independently.

### 3.4. Computational method

The geometries of bare IPC4 and its complex with  $\text{Cr}^{3+}$  cation in the gas phase were optimized based on the density functional theory (DFT) and the B3LYP/3-21G basis set by applying the GAUSSIAN 09 software package (Fig. 4). Some of the geometric selected parameters are summarized in Table 4.

It can be seen from Table 4 that the presence of DMSO results in a significantly expanded conformation of IPC4- $\text{Cr}^{3+}$  complexes compared to the presence of THF solvent and gas phase, which leads to a strongly collapsed configuration. The molecular shape of the resulted complexes can be mainly dominated by the presence of polar groups in the polar solvents that is explained by the Flory-Huggins theory [52]. According to this theory, for strongly varying dielectric constants, as given for the different solvents, one would expect different conformations for the polyelectrolyte in terms of favorable solvent-monomer interactions [53]. It is clear that the applicability of the Flory-Huggins theory is less obvious if apolar group like the phenyl ring alternates with polar group like the sulfone and the sulfonate group [29].

The binding energies,  $\Delta E$ s of (IPC4- $\text{Cr}^{3+}$ ) complexes in the vacuum, THF and DMSO pure solvent are expressed by the following equation [36,56]:

$$\Delta E = E_{(\text{IPC4-Cr}^{3+})} - E_{\text{IPC4}} - E_{\text{Cr}^{3+}} \quad (24)$$

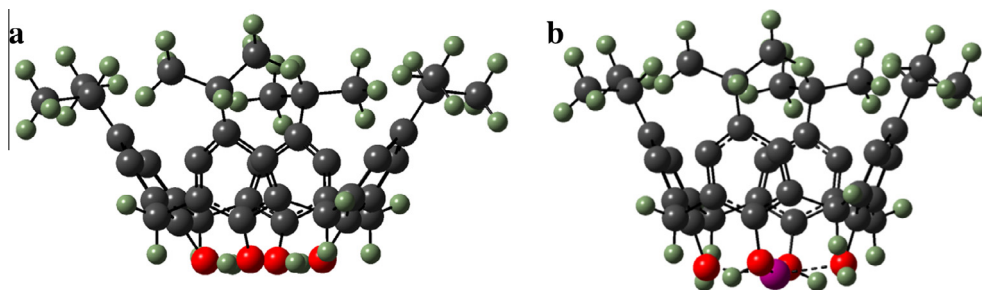
**Table 3**

Thermodynamic parameters for (IPC4- $\text{Cr}^{3+}$ ) complex in THF-DMSO binary mixed solvent.

Complex Solvent medium <sup>b</sup>	$\Delta G^\circ_c \pm SD^a$ (kJ mol <sup>-1</sup> )	$\Delta H^\circ_c \pm SD$ (kJ mol <sup>-1</sup> )	$\Delta S^\circ_c \pm SD$ (J mol <sup>-1</sup> K <sup>-1</sup> )
Pure THF	-19.11 ± 0.89	7.54 ± 2.23	89.38 ± 6.86
22.2% DMSO-77.8% THF	-17.24 ± 1.04	2.22 ± 0.39	65.27 ± 3.23
43.3% DMSO-56.7% THF	-15.99 ± 0.31	3.89 ± 0.04	66.68 ± 1.04
63.2% DMSO-36.8% THF	-15.40 ± 0.62	4.62 ± 0.34	67.15 ± 1.74
82.1% DMSO-17.9% THF	-14.59 ± 0.19	6.00 ± 1.09	69.06 ± 3.60
Pure DMSO	-15.65 ± 0.39	7.83 ± 1.31	78.75 ± 4.19

<sup>a</sup> SD = Standard deviation.

<sup>b</sup> Composition of binary mixture is expressed in mol% for solvent system.



**Fig. 4.** Optimized structure of (a) free IPC4 ligand and (b) its complex with  $\text{Cr}^{3+}$  cation.

**Table 4**

Geometric parameters for optimized free and complexed IPC4 ligand with  $\text{Cr}^{3+}$  cations.

Phase		< <sup>a</sup> OCC	<HCO	Torsion Angle of <HOCC	Atomic charge of O	<sup>b</sup> O-Cr	<COCr
Vacuum	Free ligand	121.29	112.44	153.75	-0.69	-	-
	Complex with $\text{Cr}^{3+}$	118.82	108.47	154.49	-0.62	2.21	114.59
THF	Free ligand	121.28	112.53	153.85	-0.69	-	-
	Complex with $\text{Cr}^{3+}$	109.81	114.75	170.64	-0.63	2.14	111.20
DMSO	Free ligand	121.28	112.57	153.89	-0.69	-	-
	Complex with $\text{Cr}^{3+}$	112.44	110.95	173.85	-0.62	2.12	112.96

<sup>a</sup> Angles in degrees.

<sup>b</sup> Distance in Å.

where  $E_{(IPC4-Cr^{3+})}$ ,  $E_{IPC4}$  and  $E_{Cr^{3+}}$  are electronic energies of complex, free ligand and chromium (III) cation, respectively. The calculated results of the binding energies for all complexes in the vacuum, THF and DMSO pure solvents were listed in Table 5.

Table 5 shows the electronic and binding energies of species in the gas phase, THF and DMSO pure solvents. The data shows that there is a strong infarction between the IPC4 ligand and  $Cr^{3+}$  cation in the gas phase. It is clear from Table 5 that the binding energy increases monotonically in the DMSO solvent. Therefore the binding energy of forming complex between IPC4 ligand and  $Cr^{3+}$  cation in DMSO solvent is weaker than THF solvent, showing prominent complex stability in the THF solvent. The obtained experimental data in THF and DMSO pure solvents (Table 2) shows the same trends.

### 3.5. Artificial neural network-based modeling and QP optimizer

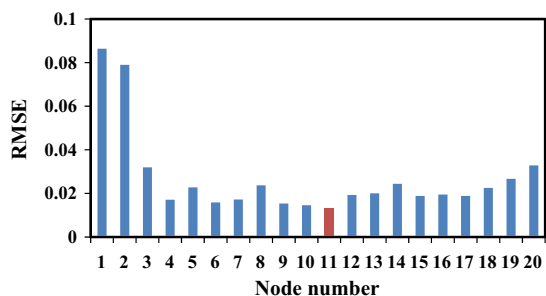
Artificial neural networks (ANNs) are computational program that can work like a human brain including the large numbers of units connected in a massively parallel structure [40,50,57]. They have a wide application in different study areas such as engineering applications, mathematics, energy systems, chemistry, physic, sensor applications, and medicine due to their advantages in estimating, eliminating and learning [41,45,46]. ANNs consist

**Table 5**

Calculated electronic energies of  $Cr^{3+}$  cation, IPC4 ligand,  $(IPC4-Cr^{3+})$  complex, and binding energies of complexes in different phase. All calculations have been done with B3LYP/3-21G basis set.

	Compounds	Electronic energy (a.u.)	Binding energy (kcal/mol)
Vacuum	$Cr^{3+}$	-1037.2198	
	IPC4	-1828.6228	
	$(IPC4-Cr^{3+})$	-2877.8362	-7526.1039
THF	$Cr^{3+}$	-1038.4613	
	IPC4	-1838.6311	
	$(IPC4-Cr^{3+})$	-2884.3722	-4568.1472
DMSO	$Cr^{3+}$	-1038.6240	
	IPC4	-1838.6335	
	$(IPC4-Cr^{3+})$	-2881.7242	-2802.8989

<sup>a</sup> 1 a.u. = 627.51 Kcal mol<sup>-1</sup>.

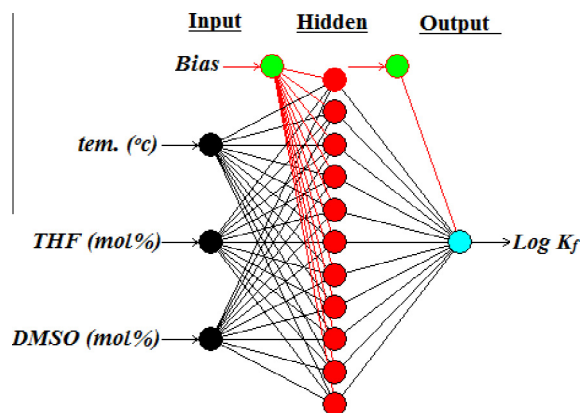


**Fig. 5.** Optimized structure of network for choosing the hidden node using the QP algorithm.

of simple nodes in parallel. These nodes are inspired by biological nervous systems. The ANN can be trained to perform a particular function by adjusting the values of the connections (weights) between nodes [47,48].

The study of complexation between macrocyclic compounds and target cations is important in all branches of chemistry and other areas. The precisions of predicted equilibriums for complex formation constant depend on the number of experimental points and relationship applied in the fitting procedure. Recently, the neural network program was proposed to evaluate the equilibrium constants from experimental data obtained by means of different experimental techniques. The proposed model allows us to predict the formation constants of studied complex reactions for given experimental conditions with sufficient accuracy [51].

The neural network applied in this study is quick propagation algorithm (QP) type with a logistic sigmoid transfer function [49]. A typical quick propagation algorithm neural network has three layers including the input, the hidden, and the output layers. In this study, thermodynamic modeling of complex reaction study in the THF–DMSO binary solvent systems at different temperatures was carried out by applying the Neural Power software version 2.525. In this model, the input layers include three nodes, temperature, the mol% of THF and mol% of DMSO in the binary mixture, the output layers includes just one node,  $K_f$  as an interesting response (Table 2). The structure of the hidden layer was determined by examining a series of topologies with varied nodes from 1 to 20. The model training was carried out to determine the root mean squared error (RMSE) as an error function by the testing data set and quick propagation algorithm (QP). The training was repeated 10 times for each node in order to avoid random correlation due to the random initialization of the weight. Among the reported results, the architectures with minimum RMSE were selected as the best topologies for each node in the hidden layer (Fig. 5). Finally, the topology with 11 nodes in a hidden layer presented the lowest RMSE which was selected as an efficient model for the stability of complex reaction between IPC4 ligand and  $Cr^{3+}$  cations. As Fig. 6 shows, the ANNs model contains three variables in



**Fig. 6.** Structure of neural network adopted in this study.



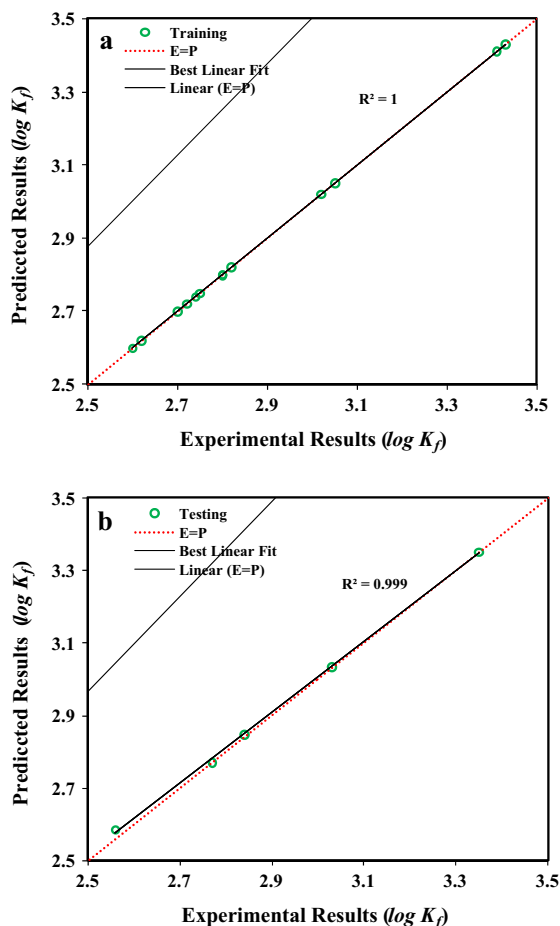


Fig. 7. Comparison of estimated  $\log K_f$  with experimental data (a) training data set and (b) test data set.

input, 11 nodes in hidden and one complex formation constant response in output layers (QP-3-11-1).

The effects of three parameters (temperature, mol% of THF in the media and mol% of DMSO in the media) for determining the complex formation ( $K_f$ ) were the input layer matrix of the network. 59 training examples and 26 testing examples and (10 times of each node) were prepared for the training, testing and validating the network, respectively. The regression coefficient of determination ( $R^2$ ) showed an excellent correlation between estimated and experimental data sets for both train (1.0) and test data sets (0.999) (Fig. 7(a) and (b)).

The obtained formation constant of complex reactions between chromium (III) cations and the IPC4 ligand using the various mol% of DMSO in THF–DMSO binary media system at different temperatures were visualized in Fig. 8 by drawing the surface and contour plots of the stability constant ( $\log K_f$ ) for the complex formation as a function of the mol% of DMSO in the binary mixtures and different temperatures.

As seen in Fig. 8, increasing the mol% of DMSO and temperatures causes to a decrease and an increase in the constant stability of complexes ( $\log K_f$ ). The maximum formation constant of complexes was obtained in zero mol percentage of DMSO (100% of THF) and the highest amount of temperature (at 45 °C). The estimated results based on the ANN program were in a good agreement with obtaining experimental results.

#### 4. Conclusions

The obtained results in the current study demonstrated that the nature and composition of the solvent system can remarkably affect the thermodynamic stability, stoichiometry, selectivity and exchange kinetics of cation-ionophore complexes and the stoichiometry of the (4-Isopropylcalix[4]arene.  $\text{Cr}^{3+}$ ) complex in all composition

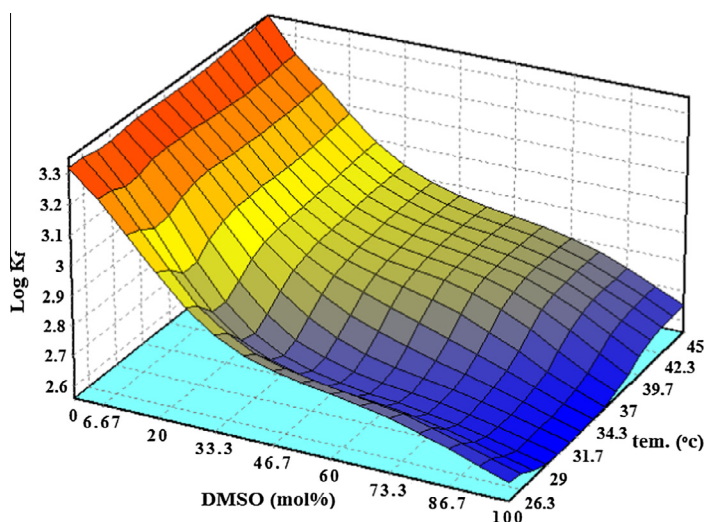


Fig. 8. Surface and contour plots of the stability constant ( $\log K_f$ ) as a function of the mole% of DMSO and temperatures.

of DMSO–THF binary mixed solvents is 1:1 [IPC4:Cr<sup>3+</sup>]. The changes in  $\Delta H^\circ_c$  for the formed complexes are negligible, whereas the changes in  $\Delta S^\circ_c$  are significant. The results obtained in this study, show that the (IPC4–Cr)<sup>3+</sup> formed complex is enthalpy destabilized, but entropy stabilized and the values of the mentioned parameters are affected strongly by the nature and composition of the binary mixed solvents. The negative values of  $\Delta G^\circ_c$  show the spontaneous process of formed complexes. The effects of mol% of DMSO and temperature of the studied complexes were investigated and high correlation between experimental data and ANN kinetic model was obtained which is a proof of high performance of conductometric method for the complex formation study.

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