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Potentiometric Studies on the Binary Complexes of *N*-[Tris(hydroxymethyl)methyl]glycine with Th^{4+}, Ce^{3+}, La^{3+}, and UO_2^{2+} and Medium Effects on a Th−Tricine Binary Complex

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The stability constants for M^{n+}−tricine binary complexes (1:1 and 1:2), where $M^{n+} = Th^{4+}$, Ce^{3+}, La^{3+}, and UO_2^{2+}, have been determined pH-metrically in aqueous media at 25 °C and in the presence of 0.10 mol dm^{-3} (KNO_3). The binary Th−tricine (1:1) complex was studied in the presence of different organic solvents as well as in the presence of different ratios of dioxane and at different temperatures. The calculated stability constants have been discussed in terms of the nature of both the metal ion and tricine. It is suggested that tricine may act as a tridentate as well as a bidentate ligand. Solvent basicity and proportion in addition to the differences in stabilization of the free base by hydrogen bonding with solvent molecules as well as the electrostatic effect are the major factors responsible for the observed high stability of the Th−tricine binary complex. The thermodynamic parameters (ΔH, ΔG, and ΔS) for the formation of 1:1 Th−tricine complex in the presence of 40% (w/w) dioxane at different temperatures (5−45 °C) were calculated.

Introduction

N-[Tris(hydroxymethyl)methyl]glycine, $(HOCH_2)_3CNHCH_2COOH$, which was first prepared by Good (1962), has proved quite useful as a buffer in the range of physiological interest (Bates et al., 1973; Crans et al., 1989; Perrin and Dempsey, 1974; Raval et al., 1989; Shibata, 1991). Tricine has been used as a buffer in animal tissue culture (Gardner, 1969), in fluorescent dye reagent for analyzing cells in urine and on measurement and resolution of small masses of protein (Barnes and Kaushal, 1986; Schaegger and Von Jagwa, 1987). $pK(N^+H_3)$, the second acid dissociation constant, and pH^* values for the standard tricine were determined by Soni and Kapoor (1981) and Roy et al. (1985, 1988). Volumetric behavior in mixed aqueous solvents and the effect of medium on the ionization process of tricine were studied by Jumean and Quaderi (1991) and El-Roudi (1995). Amino acids and metal−ligand amino acids have frequent utilization in biological and chemical applications (Crans et al., 1989; Bagger, 1987; Ho and Yut, 1982; Wright et al., 1988). Studies of tricine with several metal ions have been conducted (Kapoor et al., 1978; Sharma et al., 1986; Crans et al., 1991) using conductivity, potentiometry, and polarographic techniques.

Due to the importance of tricine and its complexes and due to the lack of studies concerning the lanthanide and actinide complexes of tricine, this paper reports on the complex formation of tricine with Th^{4+} and UO_2^{2+} as actinides and Ce^{3+} and La^{3+} as lanthanides. Moreover, Th−tricine binary complex has been studied potentiometrically: (i) in the presence of (40% w/w) of different organic solvents [ethanol (as an amphiprotic solvent), *N*,*N*-dimethylformamide (DMF; as a basic aprotic solvent), and dioxane and acetonitrile (AN; as low basic aprotic solvents)], (ii) in the presence of different proportions of dioxane, and (iii) with the thermodynamic parameters (ΔH, ΔG, and ΔS) were evaluated in the presence of 40% (w/w) dioxane in the temperature range 5−45 °C. The Irving and Rossotti pH-titration technique has been adopted to determine the formation constants corresponding to the various complexation equilibria in the presence of 0.10 mol dm^{-3}(KNO_3).

Experimental Section

Materials and Solutions. *N*-[Tris(hydroxymethyl)methyl]glycine (tricine) was A.R. product (Sigma) with a high purity and used without further purification. The organic solvents (ethanol, dimethylformamide, acetonitrile, and dioxane) were of high purity (A.R. or spectral grade products). Solutions of Th^{4+}, UO_2^{2+}, Ce^{3+}, and La^{3+} were prepared from their nitrate salts. A stock solution of tricine was prepared by dissolving an accurate amount by mass in the appropriate volume of bidistilled water. A NaOH solution (≈0.2 mol dm^{-3}) was prepared by dissolving the Analar pellets in CO_2-free bidistilled water, and the solution was standardized with a standard potassium hydrogen phthalate. A HNO_3 solution (≈0.1 mol dm^{-3}) was prepared and used after standardization. A total of 2.0 mol dm^{-3} of KNO_3 was used as a supporting electrolyte. More dilute solutions were prepared by appropriate dilutions of the corresponding stock solutions.

pH-metric Titration. The following mixtures were prepared (total volume 50 mL) and titrated individually against a standard CO_2-free NaOH solution.

(a) HNO_3 (3.3×10^{-3} mol dm^{-3}) +KNO_3 (0.10 mol dm^{-3}).

(b) Solution a in the presence of (2.0×10^{-3} mol dm^{-3}) of tricine.

(c) Solution b in the presence of either 2.0×10^{-3} or 1.0×10^{-3} mol dm^{-3} of the metal ion used.

(d) Solution b + 2.0×10^{-3} mol dm^{-3} thorium(IV) in the presence of 40% (w/w) ethanol, DMF, AN, or dioxane.

(e) Solution b + 2.0×10^{-3} mol dm^{-3} thorium(IV) in the presence of 10%, 20%, 30%, 40%, and 60% (w/w) of dioxane.

(f) Solution b + 2.0×10^{-3} mol dm^{-3} thorium(IV) in the presence of 40% (w/w) dioxane at 5, 15, 25, 35, and 45 °C.

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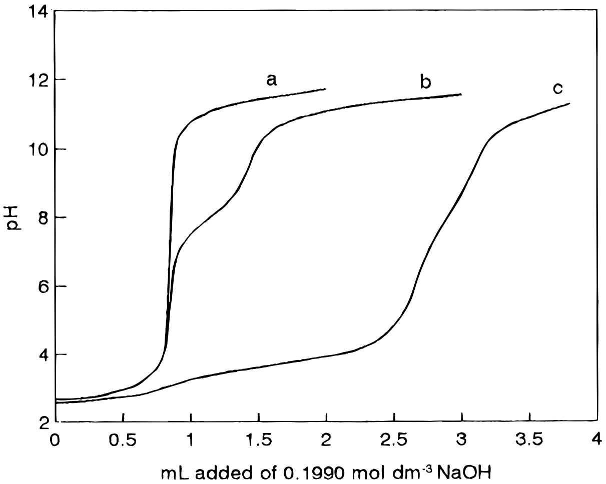

Figure 1. pH-metric titration curves for the Th−tricine (1:1) complex at 25 °C and $I = 0.10$ mol dm^{-3} KNO$_3$: (a) 0.0033 mol dm^{-3} HNO$_3$; (b) solution a + 0.002 mol dm^{-3} tricine; (c) solution b + 0.002 mol dm^{-3} Th^{4+}.

A solution a having the same proportion of organic solvent as those of c, d, and f was titrated with the base solution and used in the calculation.

pH measurements were carried out using a Fisher Scientific, Accumet pH Meter Model 825 MP. A water thermostat Fisher Scientific Isotemp Refrigerated Circulator Model 9000 accurate to ±0.1 °C was used to attain the desired temperature, where the solutions were left to stand for about 15 min before titration.

To account for the differences in acidity, basicity, dielectric constant, and ion activities for partially aqueous solutions relative to pure aqueous ones, the pH values of the former solutions were corrected by making use of the procedure described by Douhéret

$$\mathrm{pH}^* = \mathrm{pH}_{(\mathrm{R})} - \delta$$

where pH* = corrected value and pH$_{(\mathrm{R})}$ = meter readings.

The value of δ for the various proportions of each organic solvent was determined (Douhéret, 1967, 1968). The equations (Irving and Rossotti, 1953, 1954) used for various calculations were programmed using an IBM computer.

Results and Discussions

Figures 1−4 display representative sets of the experimental titration curves obtained according to the sequence described in the Experimental Section for different metal ions (Th^{4+}, UO$_2$$^{2+}$, Ce^{3+}, and La^{3+}) + tricine in molar ratios 1:1 or 1:2 in pure water, Th−tricine (1:1) in the presence of different 40% (w/w) organic solvents, Th−tricine (1:1) in the presence of different amounts of dioxane, and Th−tricine (1:1) in the presence of 40% (w/w) dioxane at different temperatures. The potentiometric titration curve of tricine (curve b, Figures 1−4) shows a sharp inflection around pH 8, indicating the dissociation of only one proton; the proton dissociation value of tricine obtained under the present experimental conditions is in agreement with the literature value (Perrin and Dempsey, 1974; El-Roudi, 1995) as given in Table 2.

Tricine, being a zwitterionic amino acid, may be expected to exist in the form of its zwitterions which may structurally be represented as

$$\underset{\mathrm{B}^-}{(\mathrm{HOH_2C})_3\text{−}\mathrm{N^+H_2}\text{−}\mathrm{CH_2COO^-}}$$

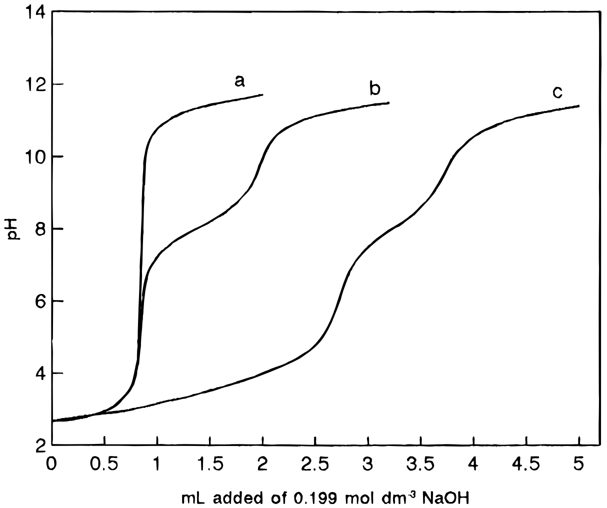

Figure 2. pH-metric titration curves for the Th−tricine (1:2) complex at 25 °C and $I = 0.10$ mol dm^{-3} KNO$_3$: (a) 0.0033 mol dm^{-3} HNO$_3$; (b) solution a + 0.004 mol dm^{-3} tricine; (c) solution b + 0.002 mol dm^{-3} Th^{4+}.

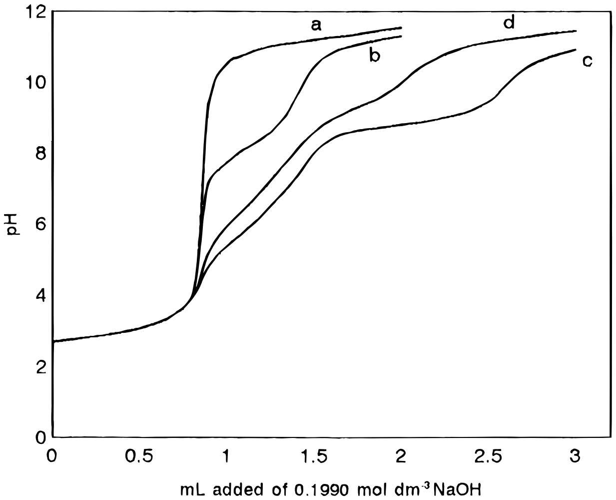

Figure 3. pH-metric titration curves for the Ce−tricine (1:1) and (1:2) complexes at 25 °C and $I = 0.1$ mol dm^{-3} KNO$_3$: (a) 0.0033 mol dm^{-3} HNO$_3$; (b) solution a + 0.002 mol dm^{-3} tricine; (c) solution b + 0.002 mol dm^{-3} Ce^{3+}; (d) solution b + 0.001 mol dm^{-3} Ce^{3+}.

It is expected to have two proton dissociation constants (in acidic media) corresponding to the cationic (≡N$^+$H) group and the carboxylic acid group, COOH. But under the present experimental conditions, only K_2(≡N$^+$H) values could be evaluated. It is possible that the hydroxyl groups are able to form a hydrogen bond with the basic nitrogen atom and thus assist in the dissociation of the ammonium hydrogen ion.

Examination of the different titration curves obtained for M−tricine solutions reveals that the equilibria involved occur in a stepwise manner. Generally, M−tricine binary complexes in different experimental conditions begin to form at pH values lower than that of free tricine (curve b). This is attained from the divergence of each of the binary M−tricine titration curves from that of the corresponding free tricine solution. The titration curves of different M−tricine (1:1 or 1:2) binary complexes in pure water showed two inflections corresponding to a stepwise release of two protons. The observed buffer zones suggest that the formed binary complexes have the tendency to undergo deprotonation of the amide group of tricine. All binary metal complex solutions under investigation show a precipitate at relatively high pH values [~10.8 and ~11.1 for

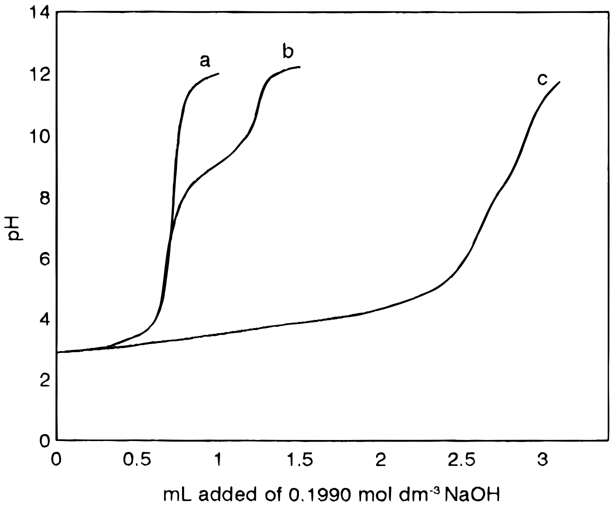

Figure 4. pH-metric titration curves for the Th−tricine (1:1) complex in the presence of 40% (w/w) dioxane at 5 °C and I = 0.10 mol dm^{-3} KNO_3: (a) 0.0033 mol dm^{-3} HNO_3; (b) solution a + 0.002 mol dm^{-3} tricine; (c) solution b + 0.002 mol dm^{-3} Th^{4+}.

La−tricine (1:1 and 1:2), ~10.9 and ~11.1 for Ce−tricine (1:1 and 1:2), ~6.5 and ~9.4 for UO_2−tricine (1:1 and 1:2), respectively], indicating that the different (1:1 or 1:2) binary complexes in pure water have a tendency to form hydroxo complex species. One can suggest that tricine chelates through carboxylic oxygen and amide nitrogen. Thus, tricine acts as an ON bidentate ligand, and the stepwise equilibria can be represented as follows:

(i) M−tricine (1:1) in pure aqueous medium

$$M^{n+} + H_2L \rightleftharpoons [M(HL)]^{(n-1)+} + H^+$$

$$[M(HL)]^{(n-1)+} \rightleftharpoons [M(L)]^{(n-2)+} + H^+$$

where M = La^{3+}, Ce^{3+}, and UO_2^{2+}.

(ii) M−tricine (1:2) in pure aqueous medium

$$M^{n+} + 2H_2L \rightleftharpoons [M(HL)_2]^{(n-2)+} + 2H^+$$

$$[M(HL)_2]^{(n-2)+} \rightleftharpoons [M(L)_2]^{(n-4)+} + 2H^+$$

where M = La^{3+}, Ce^{3+}, UO_2^{2+}, and Th^{4+}.

On the other hand, for Th−tricine (1:1 or 1:2), the titration curves do not show any precipitation, but instead three inflections in the former and two inflections in the latter are observed, respectively. So, it may be suggested that, in the case of Th−tricine (1:1), tricine chelates through one of the $(-CH_2OH)_3$ alcoholic oxygens in addition to the carboxylic oxygen and the amide nitrogen. Thus, tricine acts as a OON tridentate ligand, and the stepwise equilibria can be represented as follows:

$$Th^{4+} + H_3L \rightleftharpoons [Th(H_2L)]^{3+} + H^+$$

$$[Th(H_2L)]^{3+} \rightleftharpoons [Th(HL)]^{2+} + H^+$$

$$[Th(HL)]^{2+} \rightleftharpoons [Th(L)]^{+} + H^+$$

Th−tricine (1:1) titration curves in the presence of (40% (w/w) EtOH, DMF, and AN showed only one inflection, and a precipitate has been formed at pHs ~8.5, ~5.2, and ~8.0 in the presence of EtOH, DMF, and AN, respectively. However, the titration curve for 1:1 binary Th−tricine in the presence of 40% dioxane reflects two inflections where no precipitate is formed, indicating a tendency for deprotonation of the amide nitrogen and that the complex formed does not undergo hydrolysis. Moreover, for the titration curves of 1:1 Th−tricine, in the presence of different amounts of dioxane, two inflections appeared. Furthermore, the titration curves of the 1:1 binary Th−tricine complex solution in the presence of 40% (w/w) dioxane were selected for studying the effect of temperature on the formed complex.

Table 1. Formation Constant Values of M^{n+}−Tricine (1:1) and (1:2) Binary Complexes at 25 °C and I = 0.1 mol dm^{-3} KNO_3 in a Pure Aqueous Medium

metal	$\log K^{M}_{M-tricine}$ 1:1	1:2
Th^{4+}	8.05 ± 0.02	7.69 ± 0.03
UO_2^{2+}	6.84 ± 0.01	6.27 ± 0.04
Ce^{3+}	5.41 ± 0.007	5.14 ± 0.02
La^{3+}	5.02 ± 0.005	4.21 ± 0.01

Formation Constant Values. The horizontal distance between curves a and b; b and c; and b and d were used for the calculations of (i) acid dissociation constant values of tricine under different experimental conditions, (ii) the stability constants of M−tricine (1:1) and (1:2), and (iii) the stability constants of Th−tricine (1:1) under different experimental conditions. The equation used for the calculation of n was the same as that reported in the original papers (Irving and Rossotti, 1953, 1954):

$$\bar{n} = \frac{[(V_c - V_b)\,\text{or}\,(V_d - V_b)][C_a + C_b + C_L(y - \bar{n}_H)]}{[(V_0 + V_c)\,\text{or}\,(V_0 + V_d)]\bar{n}_H C_M}$$

Here $\bar{n}$ is the average number of ligand molecules coordinated to the metal ion, C_M is the concentration of M^{n+} used, C_L is the concentration of the ligand, y, = number of dissociable protons, and V_0 = the original volume (50 cm^3). V_b , V_c, and V_d are the volumes of alkali (NaOH) consumed to reach the same pH values in curves b−d, respectively. C_a and C_b are the concentrations of HNO_3 and NaOH, respectively. $\bar{n}_H$ values (the average number of protons associated with the ligand) for tricine at different pH values were available from determination of its formation constants. The $\bar{n}$ values were $1 \le \bar{n} \le 2$. Thus, $\bar{n}$ values do not exceed unity and 2 for M^{n+}−tricine (1:1) and (1:2) binary complexes, respectively, indicating that only one molecule of tricine combines with the metal ion in the former, whereas two molecules of tricine combine with the metal ion in the later. The free ligand exponent, pL, was calculated from the so-obtained values of $\bar{n}$ by the equation

$$pL = \log\left\{\frac{\sum_{y=0}^{y=1}\beta_y^{H}\left(\frac{1}{10^{B}}\right)}{C_L - \bar{n}_H C_M}\,\frac{V_0 + (V_c\,\text{or}\,V_d)}{V_0}\right\}$$

where β_y^{H} the formation constant value of tricine and B is the pH value. Other terms have the same meaning as defined above. The mean pK_a and $\log K^{M}_{M-tricine}$ values obtained from the corresponding experimental formation curves using the average value and straight line methods along with the error as obtained by applying least-square fits are given in Tables 1−4. The data cited in Table 1 show that $\log K^{M}_{M-tricine}$, in terms of the nature of the metal ion, follows the order $La^{3+} < Ce^{3+} < UO_2^{2+} < Th^{4+}$. This is in line with the fact that the actinides have much higher densities and a much greater tendency to form complexes compared with lanthanides (Lee, 1991). Thus, in actinides the 5f orbitals extend into space beyond the 6s and 6p orbitals and participate in bonding. This is in contrast to

Table 2. Formation Constant Values of 1:1 Th−Tricine Binary Complex at 25 °C and $I = 0.1$ mol dm^{-3} KNO_3 in Different Organic Solvents (40% w/w)

solvent	log $K^{Th}_{Th-tricine}$	$(pK_a)^a$
H_2O		8.20 $(8.15)^b$
ethanol	8.36 ± 0.05	8.37 ± 0.07 $(8.46)^c$
DMF	8.41 ± 0.06	8.52 ± 0.03 $(8.67)^c$
dioxane	8.69 ± 0.01	8.65 ± 0.05 $(8.70)^c$
AN	8.89 ± 0.03	8.85 ± 0.02 $(8.94)^c$

[a] Values within parentheses are the literature values. [b] From Perrin and Dempsey, 1974. [c] From El-Roudi, 1995, at 20 °C.

Table 3. Formation Constant Values of a (1:1) Th−Tricine Binary Complex formed at 25 °C and $I = 0.1$ mol dm^{-3} KNO_3 in Different Ratios of Dioxane

mole fraction of organic solvent	dielectric constant of the medium	log $K^{Th}_{Th-tricine}$	$(pK_a)^a$
0.0222	76.72	8.21 ± 0.06	
0.0486	74.70	8.42 ± 0.01	8.46 ± 0.05 $(8.55)^b$
0.08	72.31	8.51 ± 0.02	8.58 ± 0.07 $(8.63)^b$
0.12	69.26	8.69 ± 0.01	8.65 ± 0.05 $(8.70)^b$
0.235	60.51	8.81 ± 0.05	

Table 4. Formation Constant Values and Some Thermodynamic Characteristics of 1:1 Th−Tricine Binary Complex at $I = 0.1$ mol dm^{-3} KNO_3 in 40% (w/w) Dioxane

temp (°C)	log $K^{Th}_{Th-tricine}$	$-\Delta H$ (kJ·mol^{-1})	ΔS (J·mol^{-1}·K^{-1})	$-\Delta G$ (kJ·mol^{-1})	$(pK_a)^a$
45	8.13 ± 0.04	33.054	51.714	49.496	8.28 ± 0.04
35	8.36 ± 0.04		52.718	49.287	8.36 ± 0.06
25	8.69 ± 0.01		55.479	49.580	8.65± 0.05 $(8.70)^b$
15	8.75 ± 0.05		52.760	48.241	8.83 ± 0.04
5	8.98 ± 0.06		52.927	47.781	9.19 ± 0.07

[a] Values within parentheses are the literature values. [b] From El-Roudi, 1995, at 20 °C.

the lanthanides in which 4f orbitals are buried deep inside the atom, totally shielded by outer orbitals and thus unable to take part in bonding. For lanthanides used, log $K^{Ce}_{Ce-tricine}$ > log $K^{La}_{La-tricine}$. This is due to the smaller ionic size of Ce^{3+} (1.020 Å) than that of La^{3+} (1.032 Å) and the less basicity of Ce^{3+} than La^{3+}. For actinides used, it was found that log $K^{M}_{M-tricine}$ < log $K^{Th}_{Th-tricine}$; this is may be due to the smaller charge of the linear $(O{=}U{=}O)^{2+}$ ion with which tricine acts as a bidentate ligand, where, in the case of Th^{4+}, it can be suggested that tricine behaves as a tridentate ligand; thus, the formed 1:1 or 1:2 Th−tricine binary complexes do not undergo hydrolysis, giving the highest formation constant compared with the other metal ions. Therefore, Th−tricine (1:1) was selected for further study (effect of different organic solvents, effect of different proportions of dioxane, and effect of temperature (in the presence of 40% (w/w) dioxane)).

The dielectric constant (Charlot and Trimillon, 1969), hydrogen bonding, solvent basicity, dispersion forces, and proton−solvent interaction effects are commonly recognized as influencing factors in the ionization constant of a ligand in partial aqueous medium (Ritchie, 1969) and consequently the stability of a M−ligand complex. For a particular composition (40% w/w) of the solvent−water mixtures (ethanol as the amphiprotic solvent), DMF (as the dipolar aprotic solvent), and AN and dioxane (as low basic aprotic solvents), both pK_a of tricine and values in the various aqua-organic solvents (Table 2) change in the following order: water < ethanol < DMF < dioxane < AN.

Thus, the increase of both the pK_a value and the stability constant values of the 1:1 Th−tricine binary complex with a decrease in both basicity and hydrogen bond donor character of the organic cosolvent is consistent with the fact that the low basicity of the organic solvent and the difference in the stabilization of the free base (B^-) by hydrogen bonding from the solvent molecule are considered as major factors responsible for the observed increase in both pK_a and log $K^{Th}_{Th-tricine}$. It was found that the pK_a and log $K^{Th}_{Th-tricine}$ values increase as the amount of dioxane increases (i.e., the dielectric constant value decreases) (Table 3); thus, the dielectric constant plays an important role in the determination of these values. It can be seen from Table 4 that the value (1:1) binary complex in the presence of 40% (w/w) dioxane is decreased with increasing the temperature. This could be ascribed to the exothermic nature of the investigated complex formation process. The values of the thermodynamic functions ΔH, ΔS and ΔG for the binary complex formation were also determined.

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