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Binary and ternary metal complexes of Congo red with amino acids

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Abstract

The stability constants of the 1:1 binary complexes of Ag^+, Ni^{2+}, Co^{2+}, Y^{3+} metal ions with glutamic acid (Glu), leucine (Leu) and Congo red (CR) and their 1:1:1 ternary complex and the protonation constants of the ligands were determined potentiometrically at a constant ionic strength of $I = 0.10\ \mathrm{mol\,dm^{-3}}$ ($NaClO_4$) in aqueous solutions at 15.0, 25.0 and 35 °C. The thermodynamic parameters ΔG^o, ΔH^o and ΔS^o were reported for the complex formation reactions. The enthalpy changes of all complexation are found to be negative but entropy changes positive. The driving forces for the formation of Ag–CR, Ni–CR, Co–CR are the enthalpy decreases. But the driving force for Y–CR is the entropy decreases. The driving force of Ni–Glu, Co–Glu, Ni–Leu and Co–Leu systems are about equally enthalpy decrease and entropy increase while Ag–Glu and Ag–Leu complexation are enthalpy stabilized. But, the driving force of Y–Glu and Y–Leu systems are the entropy increase. For formed ternary complexes the reactions are all enthalpy-driven.

Keywords: Congo red dyes; Amino acids; Thermodynamic parameters; Binary and ternary complexes; Metal complexes; Congo red complexes

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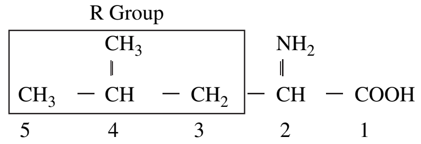
1. Introduction

In the recent decades, considerable studies have been carried out on the interaction between various metal ions and ligands that take place in biochemical processes. Furthermore, some researches focus on mixed-ligand complexes of amino acids and sulfonated azo dyes and investigations including the biological aspects have been made on the metal complex systems formed by amino acids and azo dyes [1,2].

In this work, Glutamic acid (Glu) and Leucine (Leu) were chosen as the amino acids and Congo Red (CR) as sulfonated azo dye. Leu and Glu are very important bioligands for human health.

Leu (2-amino-4 methyl pentanoic acid) is a neutral amino acid. It has one carboxyl and one amino group. Many proteins include a large amount of Leu.

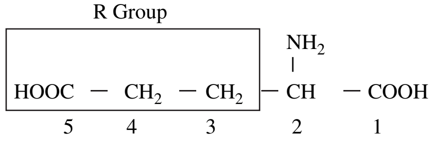
Leu



$$\mathrm{CH_3-\overset{\displaystyle CH_3}{\overset{|}{CH}}-CH_2-\overset{\displaystyle NH_2}{\overset{|}{CH}}-COOH}$$

Glu (2-aminoglutaric acid) is an acidic amino acid. It has one amino and two carboxyl groups.

Glu



$$\mathrm{HOOC-CH_2-CH_2-\overset{\displaystyle NH_2}{\overset{|}{CH}}-COOH}$$

Glu is present in the vegetable proteins such as wheat, corn, soybean, etc. The human body contains a relatively

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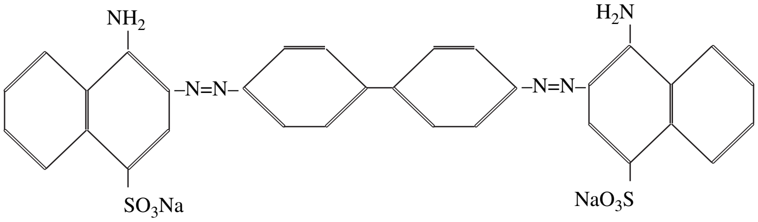
large amount of Glu. The absence of Glu in human body causes Parkinson disease [1].

CR (3,3′-[[1,1′ biphenyl]-4,4′-diylbis-(azo)] bis[4-amino-1-naphthalene-sulfonic acid] disodium salt) is a sulfonated azo dye. It has sulfonate, amino and azo groups.

CR



The sulfonated azo dyes are involved in biological processes. CR is widely used in Alzhemier's disease [3]. Amino acids such as Glu and Leu which have carboxyl and amino groups form complexes with metal ions. Similarly, CR which has azo, amino and sulfonate groups should form complexes with metal ions [4].

In this work, the stability constants of the binary and ternary complexes of Ag^+, Ni^{2+}, Co^{2+} and Y^{3+} metal ions (hereafter the charge will be omitted to prevent confusion) with Glu, Leu and CR ligands were determined from potentiometric pH titrations data at 15, 25 and 35 °C and constant ionic strength of $I = 0.1\ \text{mol dm}^{-3}$ $NaClO_4$ according to Irving–Rossotti's method [5]. As it is well known, calculations of thermodynamic functions provide a basis for interpretation of the complex formation reactions. Therefore, the enthalpy, entropy and free energy changes were calculated from the stability constants for each of the complexation reactions. The results were tried to explain according to the "hard and soft acceptors and donors (HSAB) theory".

2. Materials and methods

2.1. Material

Potentiometric measurements of the pH were performed on a titrator (Schott Titroline Alpha) with pH-combination electrode (Schott BlueLine). The electrode was also equipped with a temperature probe. The electrode system was calibrated daily with the buffer solutions prepared from Merck buffer powders at pH 4.00 and 7.00 at 25.0 °C. Potentiometric titrations were carried out in a magnetically stirred, water-jacketed cell of 100 cm^3 (Schott). It is loosely fitted with a special cover, through which could be inserted the tip of titrator's dosing unit, the electrode and nitrogen inlet and outlet tubes. By circulating water from a thermostat (Grant W14) through the jacket of the cell the temperature of the solution to be titrated was kept constant. The titrations were carried out in an inert atmosphere by bubbling purified nitrogen through the solutions.

2.2. Chemicals

Leu, Glu, CR, the nitrate salts of silver, nickel, cobalt and yttrium, sodium perchlorate, perchloric acid, sodium hydroxide (titrisol) were all pro analysi from Merck. All solutions were prepared with bidistilled, chloride and carbon dioxide-free water. The aqueous stock solutions of CR (wearing suitable protective glove, mask, glasses, etc., and storing in a special vessel), Leu and Glu were prepared daily and stored in the dark.

2.3. Measurements

The experimental procedure involved the potentiometric titration of the solutions with 0.100 mol dm^{-3} sodium hydroxide solution as listed below.

(a) $HClO_4$ (10.0 mmol dm^{-3}),
(b) $HClO_4$ (10.0 mmol dm^{-3}) + Glu (2.00 mmol dm^{-3}),
(c) $HClO_4$ (10.0 mmol dm^{-3}) + Leu (2.00 mmol dm^{-3}),
(d) $HClO_4$ (10.0 mmol dm^{-3}) + CR (2.00 mmol dm^{-3}),
(e) $HClO_4$ (10.0 mmol dm^{-3}) + Glu (2.00 mmol dm^{-3}) + CR (2.00 mmol dm^{-3}),
(f) $HClO_4$ (10.0 mmol dm^{-3}) + Leu (2.00 mmol dm^{-3}) + CR (2.00 mmol dm^{-3}),
(g) $HClO_4$ (10.0 mmol dm^{-3}) + Glu (2.00 mmol dm^{-3}) + M (2.00 mmol dm^{-3}),
(h) $HClO_4$ (10.0 mmol dm^{-3}) + Leu (2.00 mmol dm^{-3}) + M (2.00 mmol dm^{-3}),
(i) $HClO_4$ (10.0 mmol dm^{-3}) + CR (2.00 mmol dm^{-3}) + M (2.00 mmol dm^{-3}),
(j) $HClO_4$ (10.0 mmol dm^{-3}) + Glu (2.00 mmol dm^{-3}) + CR (2.00 mmol dm^{-3}) + M (2.00 mmol dm^{-3}),
(k) $HClO_4$ (10.0 mmol dm^{-3}) + Leu (2.00 mmol dm^{-3}) + CR (2.00 mmol dm^{-3}) + M (2.00 mmol dm^{-3}),

M is any one of the four metal ions. The total volume of each solution was 25 cm^3. Potentiometric measurements were carried out at 15.0, 25.0 and 35.0 °C, at an ionic strength of 100 mmol dm^{-3} maintained by addition of the appropriate amount of 1.0 mol dm^{-3} sodium perchlorate stock solution.

2.4. Calculations

The protonation constants of the ligands were calculated from the potentiometric pH titration data of the solutions from (a) to (d). First, for each ligand the values of the average proton-ligand formation number, n_A (the mean number of protons bonded) were calculated by the following equation [5,6]:

$$n_A = y + \{(v_1 - v_2)([B]+[A]_o)/(V_o + v_1)[L]_o\} \quad (1)$$

where $[B]$/mmol dm^{-3} is concentration of NaOH titrisol = 100, $[A]_o$/mmol dm^{-3} is initial concentration of $HClO_4$ solution = 10.0, $[L]_o$/mmol dm^{-3} is total ligand concentration = 2.00, V_o/cm^3 is volume of solution to be titrated = 25.0, v_1 and v_2/cm^3 are volumes of NaOH read directly from titration curves (or were calculated by a PC using MS Excel) for the same pH value, and y is number of dissociated hydrogen of ligand: 0 for CR, 1 for Leu, and 2 for Glu.

Then the curve of $n_A = f(pH)$ was plotted and the values of protonation constants (pK_a) were read directly from the titration curve of M-ligand (or were calculated by a PC using MS Excel) at $n_A = 0.5, 1.5, \ldots$ [5].

The stability constants of the complexes were calculated from the potentiometric pH titration data of the solutions from (e) to (k). For this calculation, the average metal ion–ligand (or ligands) formation number, n_L, at various pH was determined (Eq. (2)) [5].

$$n_L = (v_1 - v_2)([B]+[A]_o) + [L]_o(y - n_A)/(V_o + v_3)n_A[M]_o \quad (2)$$

where $[M]_o$/mmol dm^{-3} is total metal concentration = 2.00, v_3/cm^3 is the volume of NaOH read directly from titration curve (or was calculated by a PC using MS Excel) for the same pH value as that of v_1 and v_2 and the other symbols are as mentioned above.

Then pL (the free ligand exponent) values were calculated using Eq. (3) [5].

$$pL = \log\left\{(1 + \beta_1[H^+] + \beta_2[H^+]^2 + \beta_3[H^+]^3 \ldots)/([L]_o - n_L[M]_o)\right\} \quad (3)$$

Here, $\beta_1 = K^{H}_{HL}, \beta_2 = K^{H}_{HL}K^{HL}_{H_2L}, \beta_3 = K^{H}_{HL}K^{HL}_{H_2L}K^{H_2L}_{H_3L}, \ldots$. Finally, by utilizing corresponding values of n_L and pL, the formation curve of the metal ion–ligand system was drawn and the stability constant was read directly (or was calculated by a PC using MS Excel) at $n_L = 0.5$.

Assuming that the enthalpy change, ΔH^o, is constant in the range of temperature studied, ΔH^o of the ligand protonation and complex formation reactions were calculated from Eq. (4) [6].

$$\ln K = (-\Delta H^o/RT) + I \quad (4)$$

The free energy changes, ΔG^o, and the entropy changes, ΔS^o, were calculated from the stability constants according to Eqs. (5) and (6).

$$\Delta G^o = -RT\ln K \quad (5)$$

$$\Delta S^o = (\Delta G^o - \Delta H^o)/T \quad (6)$$

where $\ln K$ is stability constant, R is gas constant (8.314 J K^{-1} mol^{-1}), and T/K is temperature.

3. Results and discussion

3.1. Proton–ligand system

The potentiometric titration curves of the ligands at 25 °C are shown in Figs. 1–3. The moles of NaOH (n) added after neutralization of $HClO_4$ is also indicated in the figures. Similar titration curves were obtained at the other temperatures studied. Each curve exhibits an inflection at a point corresponding to the concentration of protons dissociated as expected and previously reported. The buffer regions between $n = 0$ and 1, and $n = 1$ and 2 for Glu are indicative of dissociation of proton from R group of Glu (i.e. –COOH of R) and $-\overset{+}{N}H_3$ groups of Glu [1]. The buffer region between $n = 0$ and 1 for Leu is indicated of dissociation of

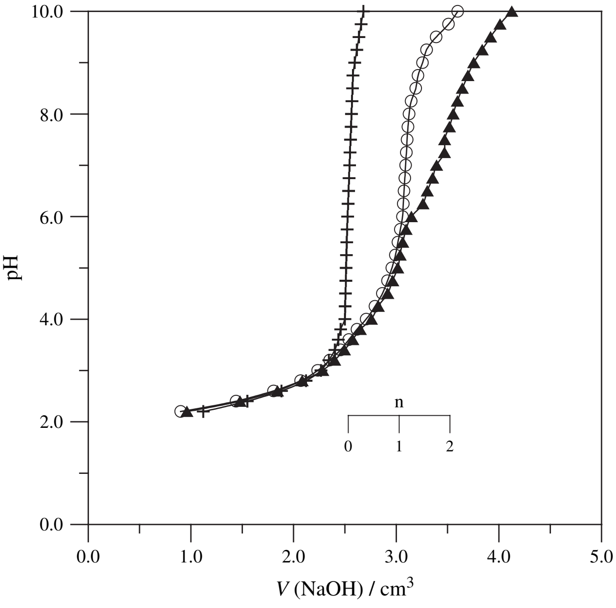


Fig. 1. Potentiometric titration curves of: (+) $HClO_4$, (○) $HClO_4$ + Glu, and (▲) $HClO_4$ + Glu + Ni at 25.0 °C.

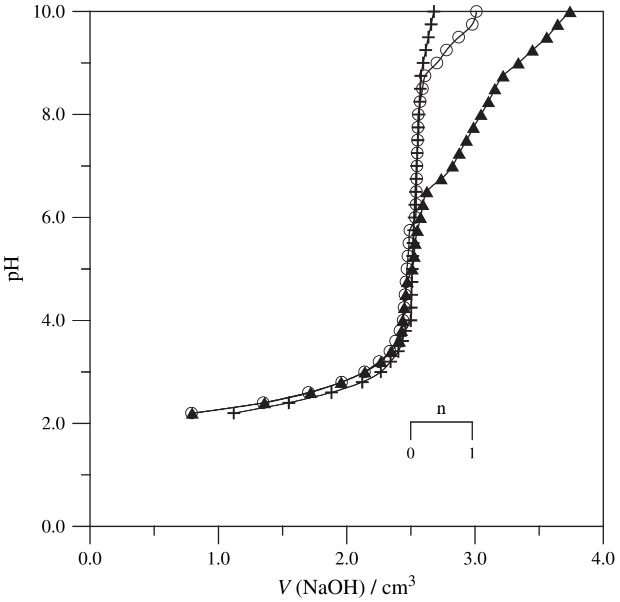


Fig. 2. Potentiometric titration curves of: (+) $HClO_4$, (○) $HClO_4$ + Leu, and (▲) $HClO_4$ + Leu + Ni at 25.0 °C.

proton from $-\overset{+}{N}H_3$ group of Leu and the buffer region between $n = -2$ and 0 for CR is indicative of the dissociation of protons from protonated CR ($-\overset{+}{N}H_3$ groups). Glu gave two protons and Leu gave one during the titrations. Therefore, two protonation constants (pK_R and pK_{NH_2}) were determined for Glu and one (pK_{NH_2}) for Leu (pK_{COOH} of Glu and Leu could not be determined; they were calculated approximately from the relationship of $pK_{COOH} + pK_{NH_2} = 2pH$ at $n_A = 1$) in this study. Protonated CR has two protons, but one protonation constant was obtained due to the fully symmetric structure of CR molecule. The determined values of protonation constants and thermodynamic parameters are given in Tables 1 and 2. The protonation constants of each ligand decreased with increasing temperature. Therefore corresponding enthalpy changes are exothermic.

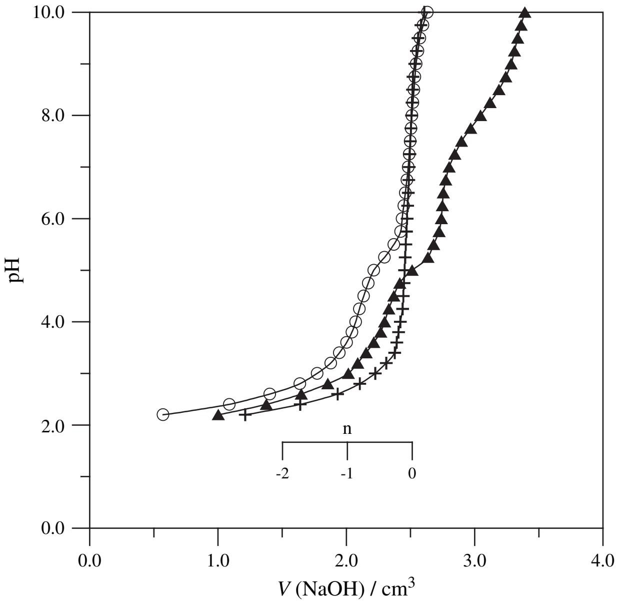


Fig. 3. Potentiometric titration curves of: (+) $HClO_4$, (○) $HClO_4$ + CR, and (▲) $HClO_4$ + CR+ Ni at 25.0 °C.

3.2. Binary complex systems

The potentiometric titration curves of Ni–Glu, Ni–Leu and Ni–CR systems at 25 °C are shown in Figs. 1–3. In all titration curves the ligand and M–ligand curves were sufficiently separated to give complexes. Similar titration curves were obtained at the other metal ions and temperatures studied. The color of the solution was light green for Ni–Glu and Ni–Leu systems at pH between 5.75 and 7.5 and 4.25 and 7.5, respectively. But the color of the solution (colorless at the beginning) was slightly changed during the titrations for the other M–Glu and M–Leu systems. For M–CR, M–Glu–CR and M–Leu–CR systems the characteristic colors of CR indicator were observed during the titrations. No precipitation occurred in solutions of all the systems during the titrations. The calculated stability constants of 1:1 binary complexes of Glu, Leu and CR with Ag, Ni, Co, Y metal ions and the thermodynamic parameters are presented (Tables 3–8).

As it is well known, HSAB theory classifies acceptors (metal ions, proton) and donors (Ligands: Glu, Leu, CR, etc.) as hard or soft based on their thermodynamic behaviors (or coordination affinities) in aqueous solutions. The simple rule of this useful theory is 'hard acceptors prefer hard donors and soft acceptors prefer soft donors' [7]. According to this classification, Y is a hard and Ag is a soft acceptor, but Ni and Co are at the border-line between these two classes like many acceptors (and donors). On the other hand, Glu and Leu possess two different donor atoms: N (of amino group) and O (of carboxyl group); and O is harder than N [8]. Therefore during complexation with Glu or Leu, Ag prefers N donor atom but Ni, Co and Y may prefer both

Table 1
Protonation constants, pK_a, of the ligands at $I = 0.10$ mol dm^{-3} ($NaClO_4$)

Ligands	pK_a	15 °C	25 °C	35 °C
Glu	pK_{COOH}		2.2[a]	
	pK_R	4.25	4.18	4.12
	pK_{NH_2}	9.66	9.51	9.37
Leu	pK_{COOH}		2.3[a]	
	pK_{NH_2}	9.66	9.54	9.42
CR	pK_{NH_2}	5.37	4.93	4.52

[a] Calculated approximately.

Table 2
Thermodynamic parameters for the proton–ligand systems

Ligands	pK_a	ΔH^o/kJ mol^{-1}, 15.0–35.0 °C	ΔG^o/kJ mol^{-1}, 25.0 °C	ΔS^o/J K^{-1} mol^{-1}, 25.0 °C
Glu	pK_R	−10 (44%)	−24	46
	pK_{NH_2}	−25 (47%)	−54	99
Leu	pK_{NH_2}	−20 (38%)	−55	114
CR	pK_{NH_2}	−72 (100%)	−28	−148

Table 3
Stability constants, log K^M_{ML}, of 1:1 M–Glu binary complexes at $I = 0.10$ mol dm^{-3} (NaClO$_4$)

M ion	T/°C		
	15.0	25.0	35.0
Ag	3.92	3.85	3.78
Ni	5.98	5.87	5.79
Co	4.74	4.68	4.62
Y	6.05	5.98	5.91

Table 4
Stability constants, log K^M_{ML}, of 1:1 M–Leu binary complexes at $I = 0.10$ mol dm^{-3} (NaClO$_4$)

M ion	T/°C		
	15.0	25.0	35.0
Ag	4.09	3.98	
Ni	5.69	5.62	5.54
Co	4.38	4.31	4.24
Y	5.98	5.93	5.87

Table 5
Stability constants, log K^M_{ML}, of 1:1 M–CR binary complexes at $I = 0.10$ mol dm^{-3} (NaClO$_4$)

M ion	T/°C		
	15.0	25.0	35.0
Ag	3.90	3.78	
Ni	5.15	5.06	4.96
Co	3.24	3.17	3.10
Y	3.19	3.14	3.09

Table 6
Thermodynamic parameters for 1:1 M–Glu systems

M ion	ΔH^o/kJ mol^{-1}, 15.0–35.0 °C	ΔG^o/kJ mol^{-1}, 25.0 °C	ΔS^o/J K^{-1} mol^{-1}, 25.0 °C
Ag	−13 (62%)	−22	31
Ni	−16 (47%)	−34	59
Co	−11 (43%)	−27	52
Y	−11 (31%)	−34	77

The figures in parenthesis are the percent contributions of the enthalpy change to the free energy decrease.

Table 7
Thermodynamic parameters for 1:1 M–Leu systems

M ion	ΔH^o/kJ mol^{-1}, 15.0–35.0 °C	ΔG^o/kJ mol^{-1}, 25.0 °C	ΔS^o/J K^{-1} mol^{-1}, 25.0 °C
Ag	−18 (77%)	−23	16
Ni	−14 (46%)	−32	62
Co	−12 (46%)	−25	43
Y	−10 (30%)	−34	80

N and O. CR possesses also two different donor atoms; N (of amino or azo groups) and O (of sulfonate groups). These donor atoms may be involved in complexation of CR with metal ions. Thus, it is known that metal complexation occurs through the azo groups for many azo dyes [9]. However, negatively charged sulfonate groups make the ligands and their complexes soluble in water [9].

The stability constants of all the 1:1 binary complex systems decreased with increasing temperature in aqueous solutions (Tables 3–5). Corresponding enthalpy changes are exothermic (Tables 6–8). For Ni–Glu, Co–Glu, Ni–Leu and Co–Leu systems (interaction between acceptor and donor of medium hardness) the driving force is about 45% enthalpy decrease and 55% entropy increase (Tables 6 and 7). For Y–Glu and Y–Leu systems the driving force is the entropy increase (interaction between hard acceptor and donor of medium hardness) and a minor contribution to the stability of these complexes also comes from the enthalpy decrease: approximately 30%. Ag–Glu and Ag–Leu complexation are enthalpy stabilized (interaction between soft acceptor and donor of medium hardness). A minor contribution comes from the entropy increase: approximately 38% and 25%, respectively. For Ag–CR, Ni–CR and Co–CR systems the enthalpy changes contribute greater than 50% to the decrease in free energy. This may be attributed to the relatively softer character of these acceptors and CR donor in aqueous medium. For Y–CR system the entropy increase contributes greater than 50% to the decrease in free energy. This is due to the hardness of the Y ion. Thus, Y–CR complex is relatively weaker as expected. These thermodynamic behaviors are in good agreement with HSAB theory: for interactions between the soft (or hard) acceptors (or donors) and donors (or acceptors) of medium hardness, the driving force for the

Table 8
Thermodynamic parameters for 1:1 M–CR systems

M ion	ΔH^o/kJ mol^{-1}, 15.0–35.0 °C	ΔG^o/kJ mol^{-1}, 25.0 °C	ΔS^o/J K^{-1} mol^{-1}, 25.0 °C
Ag	−20 (94%)	−22	7
Ni	−16 (58%)	−29	43
Co	−11 (58%)	−18	23
Y	−8 (42%)	−18	34

formation of complexes is about equally enthalpy and entropy changes [7] or both enthalpy and entropy changes in general.

3.3. Ternary complex systems

The potentiometric titration curves for Ni–Glu–CR and Ni–Leu–CR systems in a 1:1:1 molar ratio at 25 °C are shown in Figs. 4 and 5. In all titration curves the ligands and M–ligands curves were sufficiently separated to give complexes. Similar titration curves were obtained at the other metal ions and temperatures studied. 1:1:1 ternary complexes of Ag were not obtained (precipitation occurred at the beginning). The calculated stability constants of 1:1:1 ternary complex of Glu, Leu and CR with metal ions and the thermodynamic parameters are presented in Tables 9–12. The stability constants decreased with increasing temperature. Therefore, corresponding enthalpy changes were exothermic. The $\Delta\log K$ values were negative (Table 13) indicating that the stabilities of these ternary systems are lower than those of the corresponding binary systems [6]. All ternary complexation were enthalpy-driven. But a minor contribution also came from the entropy change.

In ternary complexes, binding may take place via N and/or O atoms (–COOH) of the ligands to the M ion almost simultaneously (L_1–M–L_2, L_1: Glu or Leu and L_2: CR). But interactions between sulfonate groups of sulfonated azo dyes and carboxyl group of amino acids (sulfonate–carboxyl interaction) are reported as an important phenomenon in crystal structures [3] and hence, possibility of M–(L_1–L_2) binding may be taken into account. With the thermodynamic data of this study, it could not be concluded that which kind of interaction occurred. However, negative enthalpy and positive entropy changes imply the relatively softer character of the reactions. Therefore it may be concluded that N atom/atoms (of the ligand/ligands) are included beside O atom/atoms (of the ligand/ligands) in the interactions among M, L_1 and L_2. On the other hand, this situation does not effect the stability constants calculations of ternary complexation in this study.

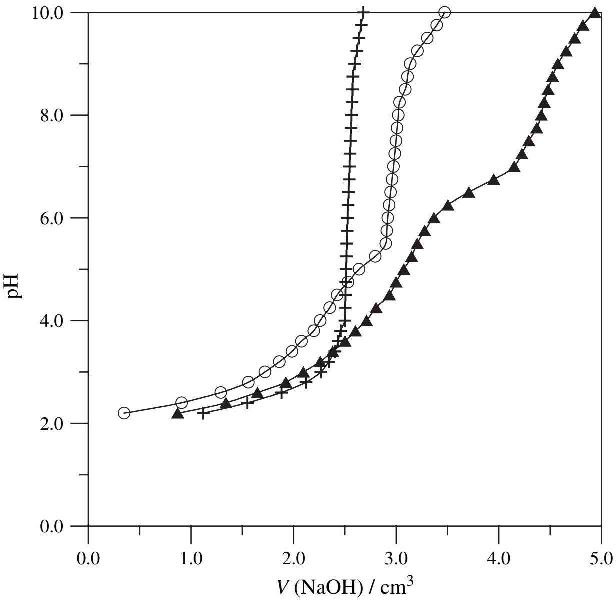


Fig. 4. Potentiometric titration curves of: (+) $HClO_4$, (○) $HClO_4$ + Glu + CR, and (▲) $HClO_4$ + Glu + CR + Ni at 25.0 °C.

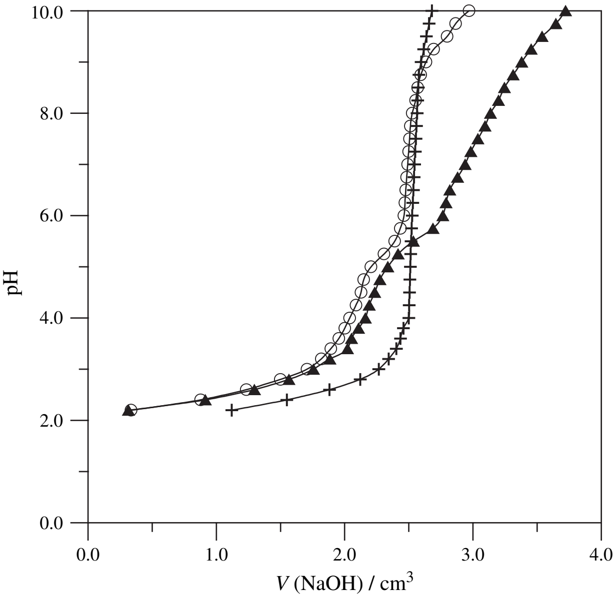


Fig. 5. Potentiometric titration curves of: (+) $HClO_4$, (○) $HClO_4$ + Leu + CR, and (▲) $HClO_4$ + Leu + CR + Ni at 25.0 °C.

4. Conclusions

The lower temperature is favorable for protonation of all the ligands of this work.

The order of increasing stabilities of M–Glu and M–Leu complexes is Ag < Co < Ni < Y.

Hard acceptors (Y, Ni) form relatively stronger complexes with Glu and Leu.

For M–CR system the order of increasing stabilities is Y < Co < Ag < Ni.

For all M–CR, M–Glu and M–Leu complexes, the increasing order of the contribution ratio of the entropy changes to the free energy decrease is Ag < Co ≤ Ni < Y. This is almost the same as the order of increasing charge/radius ratio of these acceptors, as it is known the hard acceptors have the higher values of charge/radius ratio [10,11]. Therefore, this order is the increasing hardness order

Table 9
Stability constants of 1:1:1 M–Glu–CR ternary complexes at $I = 0.10\ \mathrm{mol\ dm^{-3}}$ ($NaClO_4$)

M ion	T/°C		
	15.0	25.0	35.0
Ni	7.20	7.01	6.85
Co	4.97	4.82	4.69
Y	6.21	6.08	5.97

Table 10
Stability constants of 1:1:1 M–Leu–CR ternary complexes at $I = 0.10\ \mathrm{mol\ dm^{-3}}$ ($NaClO_4$)

M ion	T/°C		
	15.0	25.0	35.0
Ni	6.82	6.63	6.47
Co	4.67	4.53	4.43
Y	6.56	6.40	6.26

Table 11
Thermodynamic parameters for 1:1:1 M–Glu–CR systems

M ion	ΔH°/kJ mol^{-1}, 15.0–35.0 °C	ΔG°/kJ mol^{-1}, 25.0 °C	ΔS°/J K^{-1} mol^{-1}, 25.0 °C
Ni	−30 (75%)	−40	34
Co	−24 (83%)	−28	12
Y	−20 (59%)	−35	48

Table 12
Thermodynamic parameters for 1:1:1 M–Leu–CR systems

M ion	ΔH°/kJ mol^{-1}, 15.0–35.0 °C	ΔG°/kJ mol^{-1}, 25.0 °C	ΔS°/J K^{-1} mol^{-1}, 25.0 °C
Ni	−29 (76%)	−38	30
Co	−21 (80%)	−26	16
Y	−26 (68%)	−37	37

Table 13
$\Delta \log K$ values[a] of 1:1:1 M–Glu–CR and M–Leu–CR systems at $I = 0.10\ \mathrm{mol\ dm^{-3}}$ ($NaClO_4$)

System	T/°C		
	15.0	25.0	35.0
Ni–GA–CR	−4.01	−4.03	−4.04
Ni–Leu–CR	−4.02	−4.05	−4.05
Co–GA–CR	−3.02	−3.01	−3.01
Co–Leu–CR	−2.96	−2.93	−2.89
Y–GA–CR	−3.03	−3.04	−3.03
Y–Leu–CR	−2.61	−2.67	−2.70

[a] $\Delta \log K = \log K^{\mathrm{MGlu}}_{\mathrm{MGlu\,CR}} - \left(\log K^{\mathrm{M}}_{\mathrm{MGlu}} + \log K^{\mathrm{M}}_{\mathrm{MCR}}\right)$; $\Delta \log K = \log K^{\mathrm{MLeu}}_{\mathrm{MLeu\,CR}} - \left(\log K^{\mathrm{M}}_{\mathrm{MLeu}} + \log K^{\mathrm{M}}_{\mathrm{MCR}}\right)$.

at the same time. In addition, it may be concluded that increasing hardness minimizes the enthalpic contribution.

The stability constants for the 1:1:1 mixed-ligand systems of M–Glu–CR and M–Leu–CR increase in order Co < Y < Ni. The increasing order of the contribution ratio of the entropic term with the free energy decrease is Co < Ni < Y. This is the same as the order of increasing charge/radius ratio and also increasing hardness of these acceptors.

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