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# Solution state studies on thermodynamic parameters and complexation behavior of inner transition metal ions with creatinine in aqueous and mixed equilibria

Sangita Sharma *, Ashish Patel, Jasmin Bhalodia, Jayesh Ramani

*Department of Chemistry, Hemchandracharya, North Gujarat University, Patan-384 265, Gujarat, India*

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## Abstract

The determination of formation constants of binary inner transition metal complexes where M =Y(III) or La(III) or Ce(III) or Pr(III) or Nd(III) or Sm (III) or Gd (III) or Dy (III) or Th(IV) and L = Creatinine have been carried out using Irving–Rossotti titration technique in aqueous media at different temperatures and at ionic strength. To understand more about the nature of equilibrium involving inner transition metals with Creatinine, the effect of dielectric constants on the stability of these complexes at different percentage of solvent variation and at different solvent systems has been studied. The formation constant ($\log\beta_n$) have been calculated on IBM computer using BEST Program. Thermodynamic parameters ($\Delta G$, $\Delta H$ and $\Delta S$) are also evaluated, negative $\Delta G$, $\Delta H$ and $\Delta S$ values indicate that complex formation is favorable at ordinary temperatures. Species distribution curves of complexes have been plotted as function of pH using Fortran IV program SPE PLOT to visualize the equilibria systems in pH range of 2-8 pH. The order of stability for metals is Y < La < Ce < Pr < Nd < Sm < Gd < Dy < Th. This order can be explained on the basis of basicity of ligand, protonation of ligand, electronic configuration of metal ions, size and ionic potential of tripositive ion, charge/size ratio of metal ions and species distribution diagrams.

***Keywords:*** Binary complexes; Formation constant; Creatinine; Ionic strength.

## 1. Introduction

Lanthanone (III) plays an important role in various biochemical reactions [1-8]. -$NH_2$ group has a wide variety of applications in medicine, biology and other fields of chemistry [9-11]. Many binary complexes of transition and inner transition metals have been studied potentiometrically [12-16]. Creatinine is chiefly filtered by the kidney, though a small amount is actively secreted. There is little-to-no tubular reabsorption of cratinine; if the filtering of the kidney is deficient, blood levels rise. Measuring serum creatinine is a simple test and it is the most commonly used indicator of renal function. A rise in blood creatinine levels is observed only with marked damage to functioning nephrons. Therefore, this test is not suitable for detecting early stage kidney diseases. A better estimation of kidney function is given by the creatinine clearance test. Creatinine clearance can be accurately calculated using serum

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[*] Corresponding author. Tel.: +91 982 5017096.
*E-mail address:* smridhee2000@yahoo.co.in (S. Sharma)

creatinine concentration and some or all of the following variables: sex, age, weight and race as suggested by the American Diabetes Association without a 24 hour urine collection [17]. Creatinine is measured in numerous mammalian species, sometimes with the interest of determining metabolic levels. The ratio of serum urea to serum creatinine is particularly examined for terrestrial species whose activity level varies considerably [18]. Many of the properties of the inner transition metal ions and their complexes appear to lend themselves to clinical applications. The lanthanides are antimicrobial and anticoagulant substances which suppress many of the types of $Ca^{2+}$ dependent cellular activation processes that occur in diseases [19]. Lanthanides appear to accumulate in tumors or at sites of inflammation. Lanthanides are of relatively low toxicity, while their metabolism can be manipulated by the presence of specific chelators by varying the site of injection or both. Most of lanthanides are cheap, readily available and straight forward to work with [20].

So, the present study was undertaken to determine the formation constants and thermodynamic parameters of Y<La<Ce<Pr<Nd<Gd<Dy<Th complexes with creatinine at 303K, 313K, 323K ± 0.1 and at ionic strength, $\mu = 0.10$, 0.2, 0.3 and 0.4 mol $L^{-1}$ ($NaClO_4$). The nature of complexes was ascertained by species distributed curves. To derive more information somewhat detailed study is carried out on stability of these complexes in different percentage of solvent variation (10%- 30%) in methanol-water mixture and in ethanol-water, butanol-water and DMF-water mixtures.

## 2. Experimental

### 2.1. Materials

All chemicals used were analytical reagent grade. All diamines (Fluka) and lanthanide nitrates (Aldrich-USA) were used without further purification. Lanthanide solutions were acidified with accurately known amounts of $HClO_4$ to prevent hydrolysis. The exact concentrations of the solutions of the lanthanide nitrates were determined by complexometric titration with disodium salt of EDTA, using EBT indicator. All solutions were prepared in doubly distilled $CO_2$-free water. Perchloric acid was standardized with standard NaOH solution and constant ionic strength was maintained with an inert electrolyte sodium perchlorate ($NaClO_4$) (Reidol).

### 2.2. Apparatus

Potentiometric titrations were carried out with Systronics μ pH meter 361 having combined glass electrode and temperature probe with readability ± 0.1°C. Temperature was maintained with High Precision Water Bath Cat. No. MSW-274 with readability ± 0.1°C. Titrations were carried out in specially designed glass cell with magnetic stirrer in nitrogen atmosphere to avoid any side reactions.

### 2.3. Potentiometric titrations

Creatinine generally coordinates to metal ions in protonated form, that is, complexation is a proton releasing reaction. Therefore, the experimental method consisted of potentiometric titration of the ligand in the absence and presence of lanthanide ions.
The method of Bjerrum and Calvin as modified by Irving and Rossotti[21] has been used.
The following three sets were prepared for titrations:
(i) acid [ 2 milimole ]
(ii) acid [ 2 milimole ] + Creatinine [ 0.5 milimole ]
(iii) acid [ 2 milimole ] + Creatinine [ 0.5 milimole ] + metal nitrate [0.05 milimole].

Total volume used in the cell was 50 mL, ionic strength was maintained at 0.1, 0.2, 0.3, 0.4 mol $L^{-1}$ [$NaClO_4$] and temperature at 303, 313, 323 ± 0.1 K in all sets. Titrations were carried out with carbonate free standardized 0.2 mol $L^{-1}$ NaOH solution.

### *2.4. Modeling strategy*

From the above titration curves of solution (i) and (ii) protonation constants were calculated using PKAS [22] program and the results are given in Table 1. For calculation of metal ligand stability constant titration data was pruned using coordination of four ligands to metal ion and a BEST FIT model was obtained. Metal stability constants of inner transition metals with creatinine were calculated using BEST FIT models.

From the titration curves of solution (i), (ii) and (iii), the values of $\beta_n$ were calculated with BEST program [23] run on personal computer using BEST FIT model. The weighted least squares treatment determines that set of $\beta_n$ values of which the metal formation

$$U = \sum_{n=0}^{N} (y - x - nz) \qquad \beta_n \chi^n$$

nearst to zero by minimizing the formation‘s’

$$S = \sum_{l=1}^{l} U^{2} (x_i y_i z_i)$$

with respect to variation of $\beta_n$ in the above equation y is the total concentration, x is total concentration of unbound ligand, z is the total ion concentration and $\beta_n$ denotes stability constants.

We report here, the $S_{min}$ values for the different metal complexes, $S_{min}$ in the same statistical distribution as $\chi^2$ with K degrees of freedom and with weights reported in accordant with Powell and Fetcher [24, 25], $S_{min}$ can be equated to $\chi^2$. The various calculated parameters for the BEST FIT models are given in table-1. Species distribution diagram of metal–ligand systems were drawn using SPE PLOT program [26].

As the values of $pK_n$ for $ML_3$ and $ML_4$ are very small, so these have been neglected for further calculations of thermodynamic parameters and effect of dielectric constant in mixed equilibria.

## 3. Results and discussion

The results of BEST FIT model that contain type of species and overall formation constants with pH range and along with some important statistical parameters are given in Table 1. Very low statistical calculation in logβ values indicates these as BEST FIT models and precision of parameters. Small $S_{min}$ values indicate that this model is best suited for the calculations. As per Irving Rossotti technique, the ligands with one dissociable or protonable site have only one stability constant value for 1:1 metal to ligand ratio but considering maximum coordination of ligand to metal ion in present set of experimental conditions with 1:10 metal to ligand ratio, the four logβ values are obtained, out of which the $\log\beta_3$ and $\log\beta_4$ leading to pKn values do not show much difference and has very low values. So it is anticipated that two Creatinine molecules are coordination to inner transition metal ion with maximum stability constant values in present set of experimental conditions.

The formation constants of the binary complexes formed due to interaction of inner transition metal ions Y(III), La(III), Ce(III), Pr(III), Nd(III), Sm(III), Gd(III), Dy(III) and Th(IV) with creatinine were calculated by measuring the magnitude of the proton liberated during the titration of the ligand in absence and presence of metal against standard sodium hydroxide solution. In the present study, one $pK_a$ values has been obtained in strong acidic conditions but $ML_1$, $ML_2$, $ML_3$ and $ML_4$, type of complexes are calculated with highest stability for $ML_2$ type of complexes.

**Table 1**
Parameters of BEST FIT model of inner transition metal ions with Creatinine in aqueous medium at temperature 30 ± 0.1 $^oC$ and ionic strength 0.2 mol $L^{-1}$.

| Metal ion | $\log\beta_1$ | $\log\beta_2$ | $\log\beta_3$ | $\log\beta_4$ | pH scale | $S_{min}$ | No. of data points |
|---|---|---|---|---|---|---|---|
| | ($Pk_1$) | ($Pk_2$) | ($Pk_3$) | ($Pk_4$) | | | |
| Creatinine | 3.5804 | - | - | - | 2- 8 | 0.0211 | 32 |
| | (3.5804) | - | - | - | | | |
| Y(III) | 1.5770 | 3.9963 | 4.5607 | 5.1607 | 2- 9 | 0.1110 | 39 |
| | (1.5770) | (2.4193) | (0.5644) | (0.6000) | | | |
| La(III) | 1.6553 | 4.0746 | 4.6390 | 5.2390 | 2- 9 | 0.1411 | 40 |
| | (1.6553) | (2.4193) | (0.5644) | (0.6000) | | | |
| Ce(III) | 1.7780 | 4.1971 | 4.7615 | 5.3615 | 2- 9 | 0.0611 | 42 |
| | (1.7780) | (2.4193) | (0.5644) | (0.6000) | | | |
| Pr(III) | 2.0209 | 4.4402 | 5.0062 | 5.6040 | 2- 9 | 0.0101 | 38 |
| | (2.0209) | (2.4193) | (0.5644) | (0.6000) | | | |
| Nd(III) | 2.1400 | 4.5593 | 5.1237 | 5.7237 | 2- 9 | 0.1411 | 43 |
| | (2.1400) | (2.4293) | (0.5644) | (0.6000) | | | |
| Sm(III) | 2.1962 | 4.6155 | 5.1799 | 5.7799 | 2- 9 | 0.0110 | 44 |
| | (2.1962) | (2.4293) | (0.5644) | (0.6000) | | | |
| Gd(III) | 2.9601 | 5.3801 | 5.9945 | 6.5445 | 2- 9 | 0.1113 | 38 |
| | (2.1962) | (2.4293) | (0.5644) | (0.6000) | | | |
| Dy(III) | 3.2780 | 5.6973 | 6.2617 | 6.8617 | 2- 9 | 0.1411 | 40 |
| | (3.2780) | (2.4293) | (0.5644) | (0.6000) | | | |
| Th(IV) | 3.4918 | 5.9111 | 6.4755 | 7.0755 | 2- 9 | 0.0233 | 42 |
| | (3.4918) | (2.4293) | (0.5644) | (0.6000) | | | |

The values of protonation constants and metal ligand formation constant of ligand ($pK_a$) decrease with increase in ionic strength of medium, which is in agreement with Debye Huckel treatment [27]. Thermodynamic stability constant (logKº) obtained by extrapolating the linear plot of log $K_1$ vs $\sqrt{\mu}$ to zero ionic strength are given in Table 2.

**Table 2**
Formation Constants of inner transition metal complexes of Creatinine in aqueous medium at different ionic strength and at temperature 30 ± 0.1 ºC.

| Metal Ion | | Stability | ionic strength($\mu$) | | | | |
|---|---|---|---|---|---|---|---|
| | | Constant | 0.1 | 0.2 | 0.3 | 0.4 | log Kº |
| Creatinine | $pK_1$ | $\log\beta_1$ | 3.6363 | 3.5804 | 3.5209 | 3.4101 | 3.1851 |
| | | Smin | 0.8131 | 0.90211 | 0.0918 | 0.0113 | |
| Y(III) | | $\log\beta_1$ | 1.5601 | 1.5770 | 1.5901 | 1.5013 | 1.4332 |
| | | $\log\beta_2$ | 4.0131 | 3.9967 | 3.8113 | 3.7273 | |
| | | Smin | 0.1311 | 0.1110 | 0.0813 | 0.1613 | |
| La(III) | | $\log\beta_1$ | 1.6913 | 1.6553 | 1.5721 | 1.4901 | 1.5561 |
| | | $\log\beta_2$ | 4.1801 | 4.0741 | 4.3991 | 4.3701 | |
| | | Smin | 0.0131 | 0.1411 | 0.1311 | 0.0911 | |
| Ce(III) | | $\log\beta_1$ | 1.8838 | 1.7778 | 1.6909 | 1.5130 | 1.4881 |
| | | $\log\beta_2$ | 4.2906 | 4.1917 | 4.0107 | 3.8791 | |
| | | Smin | 0.0131 | 0.0611 | 0.0321 | 0.1131 | |
| Pr(III) | | $\log\beta_1$ | 2.1019 | 2.0209 | 1.9010 | 1.7501 | 1.4406 |
| | | $\log\beta_2$ | 4.5901 | 4.4402 | 4.3211 | 4.1229 | |
| | | Smin | 0.1031 | 0.4101 | 0.3203 | 0.1911 | |
| Nd(III) | | $\log\beta_1$ | 2.2419 | 2.1400 | 2.0219 | 1.9301 | 1.6180 |
| | | $\log\beta_2$ | 4.7113 | 4.5593 | 4.4012 | 4.3501 | |
| | | Smin | 0.2001 | 0.1411 | 0.3111 | 0.2011 | |
| Sm(III) | | $\log\beta_1$ | 2.2813 | 2.1962 | 2.1417 | 2.0801 | 1.6729 |
| | | $\log\beta_2$ | 4.9013 | 4.6155 | 4.4713 | 4.3289 | |
| | | Smin | 0.1131 | 0.0110 | 0.2331 | 0.2109 | |
| Gd(III) | | $\log\beta_1$ | 3.0101 | 2.9606 | 2.8111 | 2.6419 | 2.5282 |
| | | $\log\beta_2$ | 5.5301 | 5.3801 | 5.2199 | 5.1901 | |
| | | Smin | 0.0119 | 0.1113 | 0.1311 | 0.1731 | |
| Dy(III) | | $\log\beta_1$ | 3.3801 | 3.2780 | 3.1419 | 3.0713 | 2.4407 |
| | | $\log\beta_2$ | 5.7198 | 5.6115 | 5.5119 | 5.4311 | |
| | | Smin | 0.2111 | 0.1411 | 0.3101 | 0.1611 | |
| Th(IV) | | $\log\beta_1$ | 3.5601 | 3.4918 | 3.3421 | 3.2301 | 2.5873 |
| | | $\log\beta_2$ | 6.0390 | 5.9111 | 5.7811 | 5.6311 | |
| | | Smin | 0.1131 | 0.0233 | 0.1709 | 0.2111 | |

The values of stability constants in Table 2 reveal that stability constants decrease with increase in temperature along with the $pK_H$ values. The high temperatures do not favor the formation of stable complexes. There results are good agreement with those of Pitzer [28, 29]. Thermodynamic parameters were calculated and reported in Table 3.

**Table 3**
Formation constants and thermodynamic parameter of inner transition metal complexes of creatinine at ionic strength 0.2 mol $L^{-1}$ $NaClO_4$.

| Metal ion | Stability constant | Temperature | | | ΔG K.Cal.$mol^{-1}$ | | | ΔH K.Cal.$mol^{-1}$ | | ΔS K.Cal.$mol^{-1}$ | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| | | 303 K | 313 K | 323 K | 303 K | 313 K | 323 K | 303 K | 313 K | 303 K | 313 K |
| Y(III) | $\log\beta_1$ | 1.5770 | 1.4713 | 1.3811 | -2.19 | -2.10 | -2.04 | -4.58 | -4.17 | -0.0154 | -0.0135 |
| | $\log\beta_2$ | 3.9963 | 3.8901 | 3.8119 | -5.54 | -5.56 | -5.63 | -4.60 | -3.61 | -0.0151 | -0.0113 |
| | Smin | 0.1110 | 0.3476 | 0.0872 | | | | | | | |
| La(III) | $\log\beta_1$ | 1.6553 | 1.5703 | 1.4619 | -2.30 | -2.25 | -2.16 | -3.68 | -5.01 | -0.0123 | -0.0163 |
| | $\log\beta_2$ | 4.0746 | 3.9713 | 3.8914 | -5.65 | -5.68 | -5.74 | -4.48 | -3.69 | -0.0147 | -0.0116 |
| | Smin | 0.1411 | 0.0990 | 0.2113 | | | | | | | |
| Ce(III) | $\log\beta_1$ | 1.7778 | 1.6813 | 1.5703 | -2.47 | -2.40 | -2.32 | -4.18 | -5.13 | -0.0140 | -0.0167 |
| | $\log\beta_2$ | 4.1971 | 4.0891 | 3.8914 | -5.82 | -5.85 | -5.74 | -4.68 | -9.13 | -0.0154 | -0.0295 |
| | Smin | 0.0611 | 0.0346 | 0.0991 | | | | | | | |
| Pr(III) | $\log\beta_1$ | 2.0209 | 2.1893 | 2.0901 | -2.80 | -3.13 | -3.09 | -7.30 | -4.58 | 0.0252 | -0.0148 |
| | $\log\beta_2$ | 4.4402 | 3.3901 | 3.3101 | -6.16 | -4.85 | -4.89 | -45.51 | -3.70 | -0.1545 | -0.0117 |
| | Smin | 0.4101 | 0.1234 | 0.0912 | | | | | | | |
| Nd(III) | $\log\beta_1$ | 2.1400 | 2.0291 | 1.9613 | -2.97 | -2.90 | -2.90 | -4.81 | -3.13 | -0.0161 | -0.0100 |
| | $\log\beta_2$ | 4.5593 | 4.4319 | 4.3108 | -6.32 | -6.34 | -6.36 | -5.52 | -5.60 | -0.0182 | -0.0178 |
| | Smin | 0.1411 | 0.0334 | 0.8900 | | | | | | | |
| Sm(III) | $\log\beta_1$ | 2.1962 | 2.0891 | 1.9131 | -3.05 | -2.99 | -2.82 | -4.64 | -8.13 | -0.0155 | -0.0265 |
| | $\log\beta_2$ | 4.6155 | 4.5314 | 4.4109 | -6.40 | -6.48 | -6.51 | -3.65 | -5.57 | -0.0118 | -0.0177 |
| | Smin | 0.0110 | 0.0761 | 0.0542 | | | | | | | |
| Gd(III) | $\log\beta_1$ | 2.9606 | 2.8143 | 2.7909 | -4.11 | -4.03 | -4.12 | -6.34 | -1.08 | -0.0212 | -0.0032 |
| | $\log\beta_2$ | 5.3801 | 5.2119 | 5.1104 | -7.46 | -7.46 | -7.54 | -7.29 | -4.69 | -0.0241 | -0.0147 |
| | Smin | 0.1113 | 0.0456 | 0.2313 | | | | | | | |
| Dy(III) | $\log\beta_1$ | 3.2780 | 3.1873 | 3.0843 | -4.55 | -4.56 | -4.55 | -3.93 | -4.76 | -0.0129 | -0.0152 |
| | $\log\beta_2$ | 5.6973 | 5.5909 | 5.4713 | -7.90 | -8.00 | -8.08 | -4.61 | -5.53 | -0.0149 | -0.0174 |
| | Smin | 0.1411 | 0.1231 | 0.0923 | | | | | | | |
| Th(IV) | $\log\beta_1$ | 3.4918 | 3.3814 | 3.2409 | -4.84 | -4.84 | -4.78 | -4.78 | -6.49 | -0.0158 | -0.0209 |
| | $\log\beta_2$ | 5.9110 | 5.8175 | 5.7963 | -8.20 | -8.32 | -8.56 | -4.05 | -0.98 | -0.0130 | -0.0024 |
| | Smin | 0.0233 | 0.0456 | 0.0912 | | | | | | | |

The negative values of ΔG and ΔH indicate the complex formation reactions are favorable at ordinary temperature. ΔS is negative for all the complexes reveal that entropy is favorable for the formation of all these complexes. These factors indicate that these are major driving force for the formation of binary complexes. The enthalpy decrease accompanying the complexation of metal ion in solution is the characteristic property of heat of the reaction and measures entropy difference between the metal-ligand and metal-water coordinated bonds. The results obtained in the present case suggested that the metal–ligand bonds are fairly strong as evidenced by their negative enthalpy changes.

**Table 4**
Formation constants of inner transition metal complexes of creatinine in different % of solvent and in various solvent system at ionic strength $\mu = 0.1M\ NaClO_4$ and at temperature 30 ± 0.1 ºC.

| Metal ion | Stability constant | Different % solvent | | | Different solvent system | | |
|---|---|---|---|---|---|---|---|
| | | 10% MeOH | 20% MeOH | 30% MeOH | 30% EtOH | 30% BtOH | 30% DMF |
| Creatinine | $\log\beta_1$ | 3.5910 | 3.7203 | 3.8413 | 4.4013 | 4.8541 | 4.1312 |
| | Smin | 0.0131 | 0.0891 | 0.0229 | 0.3430 | 0.0423 | 0.4311 |
| Y(III) | $\log\beta_1$ | 1.8121 | 1.9401 | 2.1013 | 2.4134 | 2.8311 | 2.3110 |
| | $\log\beta_2$ | 4.0131 | 4.2311 | 4.3411 | 4.5901 | 4.6304 | 4.4113 |
| | Smin | 0.1131 | 0.2091 | 0.1311 | 0.1411 | 0.0911 | 0.0319 |
| La(III) | $\log\beta_1$ | 1.9911 | 2.1314 | 2.4380 | 2.8131 | 2.9611 | 2.6130 |
| | $\log\beta_2$ | 4.1311 | 4.2491 | 4.3101 | 4.5113 | 4.5960 | 3.9950 |
| | Smin | 0.1131 | 0.4131 | 0.0911 | 0.0311 | 0.0431 | 0.1311 |
| Ce(III) | $\log\beta_1$ | 2.1130 | 2.3141 | 2.5116 | 2.9899 | 3.1341 | 2.7430 |
| | $\log\beta_2$ | 4.2110 | 4.3019 | 4.4319 | 4.6019 | 4.7113 | 4.5199 |
| | Smin | 0.0139 | 0.1331 | 0.4130 | 0.1191 | 0.2011 | 0.3101 |
| Pr(III) | $\log\beta_1$ | 2.2913 | 2.4113 | 2.6013 | 3.2813 | 3.4310 | 2.9110 |
| | $\log\beta_2$ | 4.4713 | 4.5431 | 4.6131 | 4.7811 | 4.8511 | 4.7291 |
| | Smin | 0.1139 | 0.2101 | 0.3111 | 0.4131 | 0.5101 | 0.0031 |
| Nd(III) | $\log\beta_1$ | 2.4613 | 2.6103 | 2.8913 | 3.3313 | 3.6910 | 3.1919 |
| | $\log\beta_2$ | 4.6110 | 4.8013 | 4.9011 | 4.8999 | 4.9311 | 4.8513 |
| | Smin | 0.1131 | 0.2311 | 0.1311 | 0.4113 | 0.0511 | 0.3114 |
| Sm(III) | $\log\beta_1$ | 2.5193 | 2.7713 | 2.9403 | 3.6401 | 3.8113 | 3.4103 |
| | $\log\beta_2$ | 4.7811 | 4.8113 | 4.9190 | 4.9999 | 5.0131 | 4.9600 |
| | Smin | 0.1345 | 0.2311 | 0.4113 | 0.3929 | 0.1241 | 0.2411 |
| Gd(III) | $\log\beta_1$ | 3.0113 | 3.2141 | 3.3603 | 3.8410 | 3.9013 | 3.5143 |
| | $\log\beta_2$ | 5.4811 | 5.5319 | 5.6131 | 5.7334 | 5.8119 | 5.6477 |
| | Smin | 0.3139 | 0.1123 | 0.4114 | 0.1311 | 0.1929 | 0.2113 |
| Dy(III) | $\log\beta_1$ | 3.4193 | 3.5711 | 3.6801 | 3.9901 | 4.1013 | 3.7811 |
| | $\log\beta_2$ | 5.7411 | 5.8113 | 5.9413 | 6.3114 | 6.4341 | 6.2913 |
| | Smin | 0.0131 | 0.2131 | 0.3119 | 0.0411 | 0.2911 | 0.1319 |
| Th(IV) | $\log\beta_1$ | 3.6813 | 3.7313 | 3.8140 | 4.1390 | 4.4314 | 3.9101 |
| | $\log\beta_2$ | 6.1131 | 6.2419 | 6.2999 | 6.4112 | 6.5909 | 6.3114 |
| | Smin | 0.1141 | 0.2130 | 0.0149 | 0.1131 | 0.2119 | 0.0911 |

The entropy changes accompanying the formation of metal complexes can be related to number of reacting species in the system and changes in the solvation of reactant and product species. During formation of metal chelates in solution, the ligand species get coordinated to the solvated metal ions by displacing the water molecules from the aqua– complex, $[M(H_2O)]^{3+}$ as shown in the following equation :

$$[M^{3+}(H_2O)n] + L\,(aq) \leftrightarrows ML^{3+}\,(aq) + n\,H_2O$$

Thus there will be a decrease in number of particles in system leading to decrease in disorderliness of system. The values of protonation constant and formation constant of complexes of inner transition metal ions with creatinine at temperature 30 ± 0.1ºC and 0.2 mol L$^{-1}$ ionic strength has been evaluated in mixed aqua–organic solvents and are given in Table 4. It is clear that pK$_H$ values of ligand increases with increase in organic content of aqua–organic solvent. These may be due to decrease in dielectric constant of medium, hydrogen bonding & increase in proton solvation by organic solvent. The data in table-4 show that metal ligand formation constant increases with increase in percentage of organic solvent in medium respectively.

10 % methanol–90 % water < 20 % Methanol–80 % water < 30 % methanol–70 % water. For a particular type of compounds in various aqua–organic solvent systems, it has been observed that pK$_H$ and stability constant of metal complexes are following the order 30 % butanol >30 % ethanol > 30 % DMF >30 % methanol.

In general, stability of complexes containing O-H or N-M link increases with increase in organic solvent which is due to decrease in dielectric constant of bulk solution. As dielectric constant decreases the ion–ion interaction involving proton (or metal ion) and the ligand increases to a greater extent than ion dipole interaction between protons. Higher stability in butanol–water medium is due to decrease in hydrogen–bonded structure in water. The hydrogen bonded structure is less prevalent in butanol than either in ethanol or methanol and is absent in dimethylformamide.

The order of stability for binary complexes with respect to metal ions is found as Y< La < Ce < Pr < Nd < Sm < Gd < Dy < Th. This order can be explained by considering electronic configuration, size, ionic potential of tri positive ion and charge / size ratio.

Species distribution graphs were plotted for all the selected complexes and a representative species distribution plot is presented in Fig. 1. Species distribution study as function of pH in the range of 2-8 pointed that the formation of ML$_1$, ML$_2$, ML$_3$ and ML$_4$ started around pH ~ 2.0 and all the species are found is in the same pH range of 2- 7. As pH increases, ML$_2$ type of complexes reaches to maximum value of 70% at pH ~4.0. Other species like ML$_1$, ML$_3$ and ML$_4$ are also present in equilibrium speciation plot but their % in very less and is in the same pH range. So, it is speculated that ML$_2$ is the most dominant species in distribution plots in present set of experimental conditions.

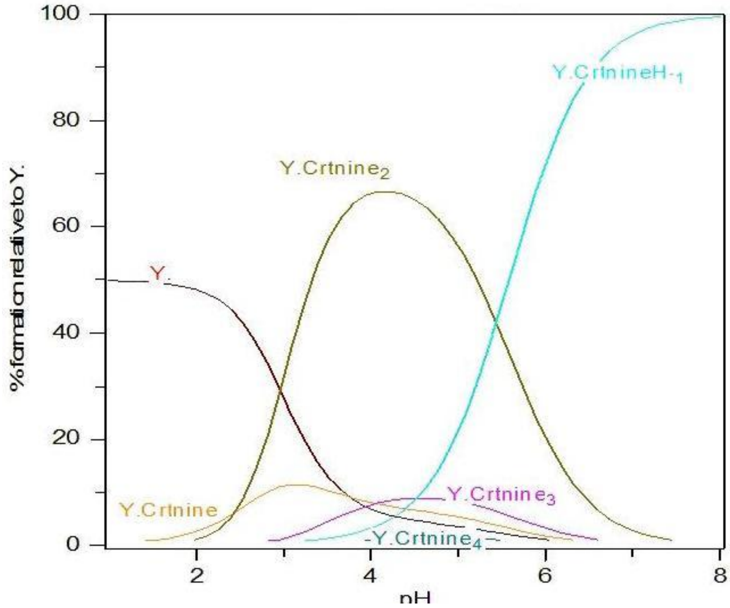

**Fig. 1.** Species distribution curves for Y(III)-Creatinine at 30$^0$C and μ=0.2M ionic strength in aqueous medium.

## 4. Conclusion

pH-metric studies on inner transition metal complexes with creatinine reveal that creatinine contain one protonable site in highly acidic medium. Species distribution plots and calculations show that $ML_1$, $ML_2$, $ML_3$ and $ML_4$ type of binary complexes are formed but species distribution plots explains for dominance of $ML_2$ type of complexes . The stability of all the analogous complexes were in order of Y(III), La(III), Ce(III), Pr(III), Nd(III), Sm(III), Gd(III), Dy(III) and Th(IV) as anticipated by increasing charge density along the series. The stability constants of the theses complexes increase as the percentage of organic solvent increases (or as dielectric constant of medium decreases) as expected from electrostatic nature of the interaction between metal ions with creatinine. Thermodynamic studies have shown that the reactions are exothermic in nature and are favoured by enthalpy change. The values of ΔS indicate that complexation reactions are entropically favoured under present experimental conditions.

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