Physico-Chemical Studies of Complexes of Trivalent Lanthanide Metal ions with 2-hydroxy phynel hydrazo dimedone in Ethanol-Water Mixed Solvent System

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The organic ligand was prepared by diazonium coupling of 2-hydroxy aniline with dimedone. Potentiometric titration used to calculate dissociation constants of this ligand in mixed solvent system (75% methanol-water) at different temperatures, the values were used in calculating the stability constants for this ligand with trivalent lanthanide metal ions in mixed solvents and constant ionic strength of 0.1M solution sodium nitrite. The effect of temperature on dissociation constants of the organic ligand and formation constants of the complexes also studied. Thermodynamic parameters were calculated using Vant-Hoff equation.

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Keywords: Thermodynamic parameters; complexation; lanthanides

1. Introduction

Dimedone is organic compound belongs to β-diketones, their keto-enol tautomerism is responsible for the formation of inner complexes with metal ions. β-diketones exists in equilibrium mixtures of keto and enol form. The nature of solvent and substituents in the methylene group has know effect on the degree of enoliztion of β-diketones. Polar solvents tend to shift the equilibrium towards the formation of diketone form while non-polar solvents like benzene increase the contents of enol form [1]. Dimedone exists in 95% enol form when water used as a solvent, which is very high as compared with acetylacetone with 15.3% in enol form. The dissociation of β-diketones is depends mainly on their structure and the nature of radical attached to the carbonyl group. Organic ligands that containing N-H group and oxygen of carboxylic acid in there chemical structure usually forms stable complexes with metal ions [2-4]. Indole-3-acetic acid, (IAA), indole-3-pyruvic acid (IPA) and indole-3-lactic acid (ILA) stability constants with some metals were tested [5].

Morgan and moss [6] first reviewed acetylacetone complexes and cited 39 known

complexes. He also reported that acetylacetone (Ac.Ac) form complexes with silver ion. Stability constants of complexes of Cu (II), Ni (II), Zn (II), and Pb (II) with Hippuric acid (II) in ethanol-water mixed solvent system at different temperatures and constant ionic strength of 0.1M solution of sodium nitrate were investigated [7]. The values of formation constants of Ac.Ac complexes with Al, Ga, In and Th using PH metric titration were reported [8]. Dissociation constant of dimedone is calculated and found to be 11.00 in 75% dioxane-water [9]. Milan Meloun studied the thermodynamic dissociation constant pKa of azathioprine was estimated by nonlinear regression of {pKa, I} pKa = 8.07 at 25℃ and 7.84 at 37℃ [10]. Lanthanide metal ions are strongly hydrated in aqueous solutions because of it is higher charge to radius ratio. The use of mixed solvents well prevents the hydration of metal ions by replacing water with solvent molecules. The formation of thermodynamically stable complexes in solution were favoured by the negative enthalpy change and positive entropy change.

The aim of this work is to study the behavior of the organic ligand with the trivalent lanthanide metal ion in mixture of 75% methanol-water and to get complete picture of the formation and the behavior of the complexes in solution and the possibilities of using these ligands for extraction of lanthanides from aqueous phase.

2. Experimental part

Most of chemicals used were of analar grade. Other materials were of highest purity available. The ligand under investigation was prepared by coupling the diazonium salt of 2-aminophenol with dimedone in sodium acetate medium to give 2-hydroxy phenyl hydrazodimedone (2-HPHD). The ligand was recrystalized several times from suitable solvent. The elemental analysis of the organic ligand showed very good agreement between the calculated and found (64.62% and 64.42%) for carbon and (6.57% and 6.35%) for hydrogen and (10.22% and 10.69%) nitrogen respectively.

The ligand posses Reddish brown color with melting point of 220°C. Methanol was boiled in presence of barium oxide under reflux until alcohol becomes yellow in color and then methanol redistilled again and used. The metal ion solution were prepared and standardized with EDTA in presence of xylenol orange indicator [10]

A digital Philips 9409-PH -meter calibrated by means of standard buffered solutions produced by BDH (England).

3. Results and discussion

The PH-metric titration curves of 2-HPHD ligand are shown in figure 1. One proton dissociate from ortho substituted between a = 0 and a = 1 (where is the number of moles of NaOH added/ mole of ligand). At higher PH values, second additional proton dissociates from hydrazo group the weak inflection at a = 2 is due to this dissociation. The first and second ionization constants calculated at different temperatures and in 75% methanol-water shown in figure 2.
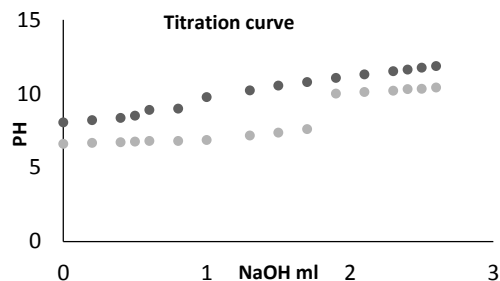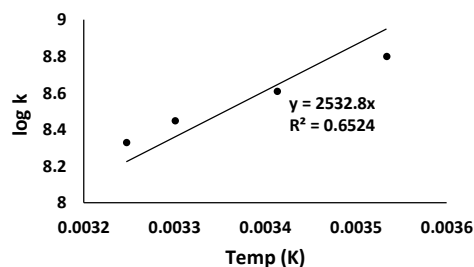

Fig.1. Ligand and metal titration curve

Fig.2. Plotting of log k Vs 1/T

Table 1 shows a set of values for first and second dissociation constants of the ligand at 30°C and I.S of 0.1M.

Table 1. Dissociation constants for the ligand at different temperatures

10°C		20°C		30°C		35°C	
PK_1	PK_2	PK_1	PK_2	PK_1	PK_2	PK_1	PK_2
8.80	11.50	8.61	11.37	8.49	11.24	8.33	11.09

Representative plot of curves of 2-HPHD with 2:1 molar ratio of ligand to Ln (III) ions were tested. The hydrolysis of these complexes occurred slowly [11,12], allowing the calculation of $logK_2$. The calculation of the over all equilibrium constants were carried out using standard procedure based on the calculation of the average number of ligand molecules bound per metal ion, n, and the free ligand concentration, A^{-2}, and then the data plotted graphically for some metal ion chelates at certain temperatures. The changes in PK values with temperature were checked using linear regression method and found to be straight line of correlation close to unity. The values decreased with increasing temperature and this indicates that raising of temperature increases the acidity of the ligand. The linear change of the stability constant values of complexes with T^{-1} permits the calculation of enthalpy change of the complexation process using Vant-Hoff's equation [13] are shown in table 2.

Table 2. calculated stability constants ($LogK_1$, $LogK_2$) values at different temperature

Ion^{+3}	10°C	20°C	30°C	35°C
La	9.78, 8.90	9.71, 8.68	9.46, 8.10	9.32, 7.76
Ce	10.81, 9.83	10.45,9.33	10.31,8.94	10.14,8.76
Pr	10.75, 9.76	10.49,9.00	10.28,8.93	10.19,8.99
Nd	10.66, 9.10	10.56,8.77	10.45,8.50	10.20,9.22

$$Log\ K = -(\Delta H/\ 2.303RT) + constant$$

Table 3 shows the results obtained by least square analysis to calculate the enthalpy change and the probable errors in enthalpy terms. The free energy change ΔG and the entropy change ΔS from the known relationships:

$$-\Delta G = 2.303RT\ logK \qquad \Delta S = (\Delta H - \Delta G)/T$$

Table 3. Thermodynamic parameters of complexation process

Ion^{+3}	$-\Delta G_1, -\Delta G_2/$ KJ mol^{-1}	$\Delta H_1, \Delta H_2/$ KJ mol^{-1}	$\Delta S_1, \Delta S_2/$ J mol^{-1}K^{-1}
La	54.88, 46.99	33.92, -----	69.19, -----
Ce	59.81, 51.87	35.97, 85.27	88.9, 12.56
Nd	60.63, 49.30	24.57, 57.44	118.09, 26.82
Sm	62.08, 51.46	38.11, 49.78	79.11, 5.54
Eu	63.24, 52.39	41.57, ----	71.52, 4.52

4. Conclusion

The results of the potentiometric studies on complexes of lanthanide metal ions with amino carboxylic acid and dimedone derivatives in mixed solvent system (ethanol-water) showed normal trend of lanthanide complexes with other organic ligands.

5. References

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