A THERMODYNAMIC STUDY OF Nd (III) CHELATES WITH BENZOYLACETANILIDE AND ACETOACETANILIDES IN ETHANOL-WATER MIXTURE

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Potentiometric equilibrium studies have been made at 20, 25, 30, 35, 40°C for benzoylacetanilide (BAA), acetoacetanilide and their neodimium (III) chelates in nonaqueous medium. The dissociation constants of these ligands were computed as well as the stability constants of their neodimium 1:1 chelates at different ionic strengths and temperatures. The free energy, ΔG, the enthalpy, ΔH and the entropy change, ΔS, for the process of the dissociation of such ligands and the formation of their Nd(III) chelates are reported in 70% (v/v) ethanol-water mixture and $0.1M$ KNO_3 ionic strength.

INTRODUCTION

There has been appreciable interest in lanthanide (III) chelates with various organic ligands[1,2]. The chelating ability of substituted benzoylacetanilides towards trivalent lanthanide and Cu(II) was studied by us[3,4].

In continuation of our studies we have investigated the thermodynamic properties like ΔG, ΔH and ΔS associated with the formation of such chelates. In this paper pH-metric investigation was made to study the conditional and thermodynamic stability constants, overall change in free energy (ΔG), enthalpy (ΔH) and entropy (ΔS) of Nd (III) complexes with benzoylacetanilides (BAA) and acetoacetanilides (AAA) in 70% (v/v) ethanol water at different temperatures.

EXPERIMENTAL

The ligands (BAA) and (AAA) were synthesized by method described[5] employing the appropriately substituded aniline. The physical constants of the compounds prepared agreed with those in literature[5]. Ethanol-water (v/v) mixtures was used in preparing potassium hydroxide (0.02 M) and potassium nitrate solutions. Stock solution of Nd (III) nitrate was prepared from the corresponding neodimium oxide (BDH Analar reagents 99.9%) and the strength of it was determined by EDTA titration using ammonium oxalate as indicator as previously described[6].

Measurement of pH were made using a Radiometer pH-meter type 63 equipped with a combined glass electrode

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type GK 2311 C. Autoburrette type Metrohn Herisau Multi-Dosimat E415, accurate to ± 0.01 ml was used. The general procedure in the titration was as previously described[3]. The pH-meter readings (B) in ethanol-water mixtures were converted into hydrogen ion concentrations by means of the equation:

$$-\log [H^+] = B + \log U_H \qquad (1)$$

where $\log U_H$ is the correction factor at a given composition of the medium at fixed temperature[7].

RESULTS AND DISCUSSION

The stiochiometric acid dissociation constant pKi of each ligand were calculated from the pH data by the equation:

$$pKi = B + \log U_H^+ + \frac{T_L - [H^+] - [KOH] + [OH^-]}{[H^+] + [KOH] - [OH^-]} \qquad (2)$$

where T_L is the analytical concentrations of the ligand. As the value of pK_w in 70% (v/v) ethanol is $\simeq 17$[8] the values of $[H^+]$ and $[OH^-]$ are very small compared with the values of $[KOH]$ and T_L. It follows that

$$pKi = B + \log U_H + \log \frac{T_L - [KOH]}{[KOH]} \qquad (3)$$

Using equation (3), the values of the pKi's for the lig-

and Ia to Ie at different temperature and the ionic strenghts were thus computed. The data were summerized in Table 1.

The stiochiometric stability constants ($\log \beta_1$) for 1:1 chelates at different temperatures and ionic strengths were computed from the titration data using the equation

$$\log \beta_1 = \log (\bar{n} / (1 - \bar{n}) - \log [L^-] \qquad (4)$$

where $[L^-]$ represents the concentration of the carbonion-enolate of the ligand used, and $\bar{n}$ is the average number of ligand molecules bound to metal ion.

$$[L^-] = \frac{K_i}{[H^+]} (TL - [KOH] - [H^+] + (OH^-) \qquad (5)$$

$$\bar{n} = T_L - [L^-] ([H^+] / Ki) + 1 / T_M \qquad (6)$$

where T_M is the analytical concentration of the metal. The values of $\bar{n}$ were calculated up to visual precipitation. For all systems examined values higher than 0.6 for $\bar{n}$ cannot be obtained, and so the stability constant β_1 for 1:1 complex species only was calculated. The assumption of the presence of 1:1 chelate over the experimental range for such systems was confirmed later(3).

For determination of the thermodynamic dissociation and chelate stability constants p^Tki and $\log {}^T\beta_1$ respectively the following equations were used.

$$pKi = p^Tki - A\mu^{1/2} \qquad (7)$$

$$\log \beta_1 = \log {}^T\beta_1 - A'\mu^{1/2} \qquad (8)$$

Where A and A′ are constants and μ is the ionic strength of the medium. Thus, the intercepts of the plots pKi and $\log \beta_1$ versus $\mu^{1/2}$ represent the values of p^TKi and $\log {}^T\beta_1$ (Calculated using the least squares methods). These results were depicted in Table 1.

The use of conditional equilibrium constant (pKi and $\log \beta_1$) rather than the thermodynamic equilibrium constants (p^TKi and $\log {}^T\beta_1$) in our discussion was justified by us (3) for similar systems.

From Table 1 it is obvious that the stability of Nd $(AAA)^{2+}$ is more than that the corresponding chelate of $Nd(BAA)^{2+}$ indicating that AAA is more basic than BAA. This makes the assumption that presence of the phenyl group is substituted β-diketones have an electron donating effect still not real. The values of stability constant for 1:1 Nd(III) chelates with BAA and AAA are comparable with that reported for $Fe(BAA)_3$ and $Fe(AAA)_3$ chelates[9].

The free energy of formation (ΔG) of the chelates has been calculated by using the equation:

$$\Delta G^\circ = - 2.303RT \log K \qquad (9)$$

For calculating the change in enthalpy (ΔH) and changes in entropy (ΔS), the stability constant of the chelates and the dissociation constant of the ligands at different temperatures have been determined.

On the other hand, the free energy is given by the sum of the enthalpy (ΔH) and an entropy term ($T\Delta S$).

$$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ \qquad (10)$$

Where T is the absolute temperature.

From the slope of the graph obtained by plotting $\log K$ against $1/T$ (Figs. 1,2) the enthalpy change (ΔH) of the

Table 1. Dissociation constants of the ligands AAA and BAA and their conditional and thermodynamic stability constants for Nd(III) chelates in 70% (v/v) ehtanol-water mixture at 30°C.

$\mu \times 10^2$	0.25	1.00	2.25	5.00	10.00	15.00	$\log {}^T\beta_1{}^b$
pKi (AAA)[a]	10.61	10.42	10.36	10.21	10.04	9.93	
pKi (BAA)[a]	9.80	9.72	9.64	9.50	9.34	9.21	
$\log \beta_1$ (Nd-AAA)[b]	–	6.33	–	6.00	5.78	5.50	
$\log \beta_1$ (Nd-BAA)[b]		5.92		5.61	5.40	5.22	
Nd-AAA							6.40
Nd-BAA							6.19

a − standard deviation in pKi, ± 0.01-0.03;   b − standard deviation in $\log \beta_1$. ± 0.05

reaction has been calculated and assuming (ΔH) to be constant over this temperature range the entropy change (ΔS) was calculated. The entropy change was also calculated from the intercept obtained by the later plot. The result obtained have been summarized in Table 2.

The negative values of ΔG, ΔH, ΔS for the dissociation of the ligands BAA and AAA (HL) ensure that the dissociation reaction:

$$HL \rightleftharpoons H^+ + L^-$$
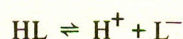
is exothermic which implies that decrease of temperature favours the dissociation of these ligands.

From the values of ΔG, ΔH and ΔS for both BAA and AAA (Table 2) it is worth mentioning that the dissociation of AAA is more sensitive to the increase of temperature than that of BAA. This may be attributed to the fact that the phenyl group of BAA is not co-planar with the enolic ring. Evaluation of this conclusion could be obtained by plotting ΔG vs. T for both BAA and AAA. Again the free energy change (ΔG) is more affected in case of AAA rather than BAA with temperature.

The thermodynamic functions of ΔG, ΔH, ΔS were also evaluated for the chelates of Nd (III) with the ligands BAA and AAA. Fig. 2 illustrates the dependence of log K_1 on the absolute temperature. The slope of straight line ob-
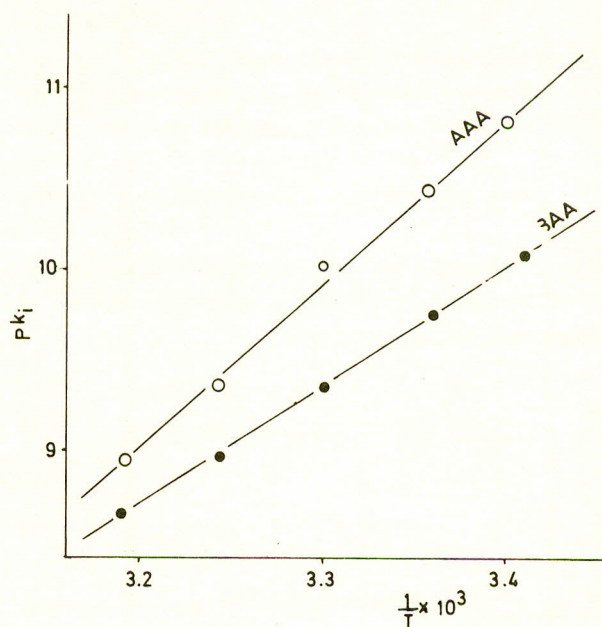
Fig. 1. Dependence of the dissociation constants pKi, for the ligands AAA and BAA upon temperature, T°K.

Table 2. Thermodynamic functions for the dissociation constants of the ligands BAA and AAA and the stability constants of their metal chelates at $\mu = 0.1M$ KNO$_3$ in 70% (v/v) ethanol-water mixture. ΔG and ΔH; K.cal/mole, ΔS; Cal/deg/mole.

		BAA	AAA	Nd(BAA)$^{2+}$	Nd(AAA)$^{2+}$
	ΔG	−13.44	−14.54	− 7.82	− 8.88
293°K	ΔH	−29.35	−39.93	−16.80	−28.92
	ΔS	−55.25	−86.63	−30.66	−68.39
	ΔG	−13.17	−14.11	− 7.67	− 8.54
298°K	ΔH	−29.35	−39.93	−16.80	−28.92
	ΔS	−54.32	−86.63	−30.66	−68.39
	ΔG	−12.89	−13.68	− 7.51	− 8.19
303°K	ΔH	−29.35	−39.93	−16.80	−28.92
	ΔS	−54.32	−86.63	−30.66	−68.39
	ΔG	−12.62	−13.25	− 7.36	− 7.86
308°K	ΔH	−29.35	−39.93	−16.80	−28.92
	ΔS	−54.32	−86.66	−30.66	−68.39
	G	−12.35	−12.81	− 7.21	− 7.51
313°K	H	−29.35	−39.93	−16.80	−28.92
	S	−54.32	−86.63	−30.66	−68.39

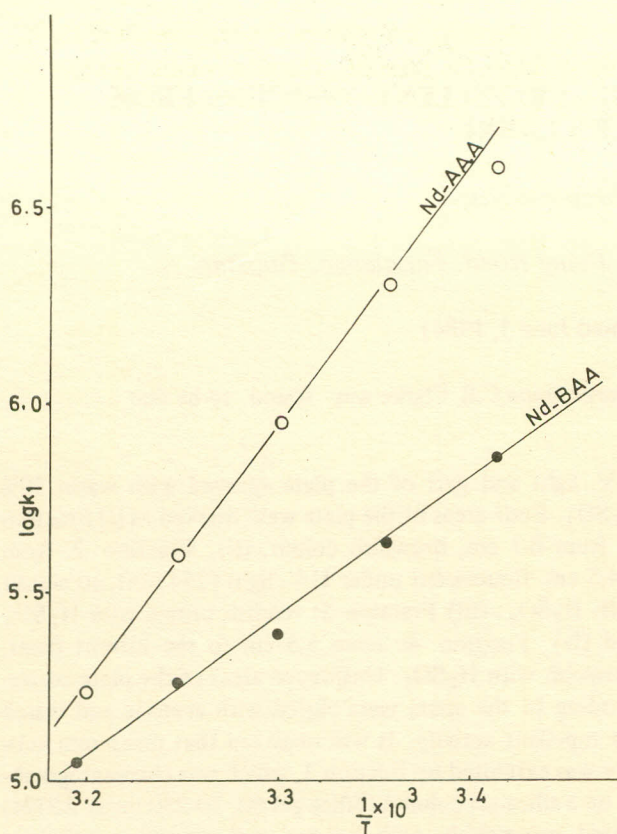Fig. 2. Dependence of the stability constant log Ki for Nd (III) chelates with AAA and BAA upon temperature T°K.

tained reveals that the formation of such chelates is highly affected by temperature. Computed values using the least squares methods of ΔG, ΔH and ΔS are depicted in Table 2. The excellent values of the correlation coefficient obtained implies that the relationship log K_1 versus $1/T$ for Nd (III) chelates with BAA and AAA are fairly correlated within the used temperatures.

Comparison of the thermodynamic functions for these chelates (Table 2) leads to the conclusion that the stability of Nd(III) chelate with AAA is higher than that with BAA. This is in accordance with our data concerning the dissociation constants of the ligands.

The negative values of ΔG, ΔH ensure that the reaction of complex formation for the investigated systems is an exothermic reaction. Consequently the reaction is more favourable at low temperatures.

The value of the entropy change, ΔS, for the studied chelates can be considered as a sum of the following entropies:

$$\Delta S = S_{Nd\ L}{}^{3-n} - S_{Nd}{}^{3+} - S_L n-$$

where $S_{Nd\ L}{}^{3-n}$, $S_{ND}{}^{3+}$, $S_L n-$ are the entropies of the complexes, the central atom and the ligands (BAA or AAA).

The values of ΔS for Nd-BAA and Nd-AAA 1:1 chelates are negative which implies that the sum $(S_{Nd}{}^{3+} + S_L 2-)$ is more negative than that of the complex species. Consequently the ordering of water or ethanol molecules around the Nd3+ in the structure of the inner sphere is more than that in case of the free Nd^{3+} ions[10]. ΔS values for Nd-AAA is more negative than that of Nd-BAA, idicating that spatial configuration of the acetyl group (CH_3-CO) is different from that of the benzoyl group (ph-co). This means that the vibrational and rotational entropies of the acetyl and benzoyl groups are different[11]

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