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Thermodynamics of Complexation of Lanthanides and Some of Transition Metal Ions by 5,5-Dimethylcyclohexane-2-(2-hydroxyphenyl)-hydrazono-1,3-dione (*DCPHD*) and Its Derivatives

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Summary. Equilibrium between *DCPHD*, *DC*-4-Cl-*PHD*, and *DC*-4-*Me*-*PHD* and protons, transition, and lanthanide ions have been investigated at 30 °C by means of potentiometric titration in 75% (*v*/*v*) methanol-water mixture containing 0.10 *M* KNO_3 as a constant ionic medium. Thermodynamic parameters (ΔG, ΔH and ΔS) referring to the formation of species HL^-, L^{--}, ML^{+n-2} and ML_2^{+n-4} (L^{--} denotes the ligand anion) have been determined in solutions. The solvent effects on the thermodynamic parameters of the complex formation are discussed in terms of differences in the donor ability of methanol and water solvents. The plots of thermodynamic parameters versus ionic potential (Z^2/r) of the lanthanide elements is not linear as expected from ionic theory. The obtained curve can be resolved in an initial group (the lighter lanthanides), an intermediate group (Sm-Dy), and a final group (the heavier ones, Tb-Lu). This behavior was explained in terms of differences in the dehydration of lighter lanthanide(III) from that of heavier ones.

Keywords. Thermodynamic parameters; 5,5-Dimethylcyclohexane-2-(2-hydroxyphenyl)-hydrazono-1,3-dione; Transition and lanthanide ions.

Thermodynamik der Komplexierung von Lanthaniden und einigen Übergangsmetall-Ionen mit 5,5-Dimethylcyclohexyl-2-(2-hydroxyphenyl)-hydrazono-1,3-dion (*DCPHD*) und seinen Derivaten

Zusammenfassung. Die Gleichgewichte zwischen *DCPHD*, *DC*-4-Cl-*PHD* und *DC*-4-*Me*-*PHD* mit Protonen, Übergangsmetall- und Lanthaniden-Ionen wurden bei 30 °C mittels potentiometrischer Titration in 75% (*v*/*v*) Methanol-Wasser mit einem Gehalt an 0.10 *M* KNO_3 als konstantem ionischem Medium untersucht. Die thermodynamischen Parameter ΔG, ΔH und ΔS zur Bildung der Spezies HL^-, L^{--}, ML^{+n-2} und ML_2^{+n-4} (L^{--} steht für das Ligandenanion) wurden in Lösung bestimmt. Die Lösungsmitteleffekte auf diese Komplexbildungsparameter werden auf Basis der Differenz im Donorvermögen von Methanol und Wasser als Solventien diskutiert. Die Diagramme der thermodynamischen Parameter gegen die ionischen Potentiale (Z^2/r) der Lanthaniden sind, wie nach der Ionentheorie zu erwarten, nicht linear. Die erhaltene Kurve läßt eine Anfangsgruppe (die leichteren Lanthaniden), eine mittlere Gruppe (Sm-Dy) und eine Endgruppe (die schwereren Lanthaniden, Tb-Lu) erkennen. Dieses Verhalten kann aus dem Unterschied im Dehydratationsverhalten erklärt werden.

Introduction

In a previous paper we reported the formation constants or Gibbs energies, enthalpies and entropies of formation of 5,5-dimethylcyclohexane-2-(2-hydroxyphenyl)-hydrazono-1,3-dione (*DCPHD*) complexes of nickel(II), neodymium(III) and ytterbium(III) ions in 75% (*v*/*v*) isopropanol-water solvent [1]. In order to provide a more complete thermodynamic characterization, this study is extended to other transition metal ions and the complete series of the lanthanide elements.

Experimental Part

5,5-Dimethylcyclohexane-2-(2-hydroxy-4-chloro-phenyl)-hydrazono-1,3-dione (*DC*-4-Cl-*PHD*), 5,5-di-methylcyclohexane-2-(2-hydroxy-4-methyl-phenyl)-hydrazono-1,3-dione (*DC*-4-*Me*-*PHD*) and *DCPHD* were prepared as described previously [1]. Reagents and procedures are essentially the same as that used in previous work [1, 2].

Results

For all ligands employed potentiometric titration curves for ligands and metal-ligand systems in 75% (*v*/*v*) methanol-water were explained by considering the diprotic nature [1, 2] of the ligands (H_2L) and the formation of two mononuclear complexes ML^{+n-2} and ML_2^{+n-4}. Typical titration curves obtained in 75% (*v*/*v*) methanol-water are shown in Fig. 1. The value of the activity coefficient $\delta \pm$ for the hydrogen ion in methanol-water was taken as 0.619 (see Ref. [3] and the protonation and stability constants of the ligands and their metal chelates were calculated as described previously [1].

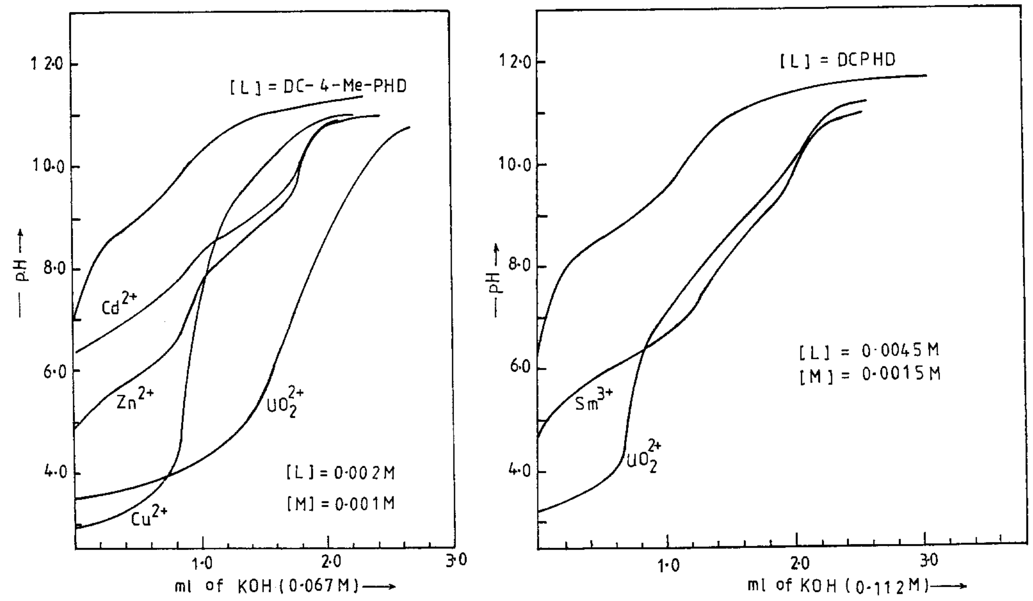

Fig. 1. Potentiometric titration curves of *DCPHD* and *DC*-4-*Me*-*PHD* in absence and presence of some metal ions ($t = 30$ °C, 75% methanol-water)

The variation of pK_1^H, pK_2^H, $\log K_1$ and $\log K_2$ versus l/T gives straight lines with correlation coefficients equal to 0.990–0.999. This linear change permits the calculation of enthalpy of complexation by the use of the Vant Hoff equation [4]. The free energy and entropy change are calculated using the known relationships as described in [4].

The protonation constants of the ligands and the stability constants of their metal chelates at different temperatures are given in Tables 1 and 3, the thermodynamic functions in Tables 2 and 4.

Discussion

Figure 2 shows a plot of ΔG vs. ΔH for the chelates of *DCPHD* and *DC-4-Me-PHD*. It can be seen that these relations are roughly linear. This is to say that the entropy changes of the reactions have caused no unusual effects within the chelates of the given reagent. It is reasonable to assume that this will generally be true; therefore the entropy of a series of chelation reactions with a given reagent will either be roughly constant or will vary regularly. This accounts for the wide spread success of $\log K_1$ vs. second ionization potential ($2Ip$) graphs shown in Fig. 2. Each time

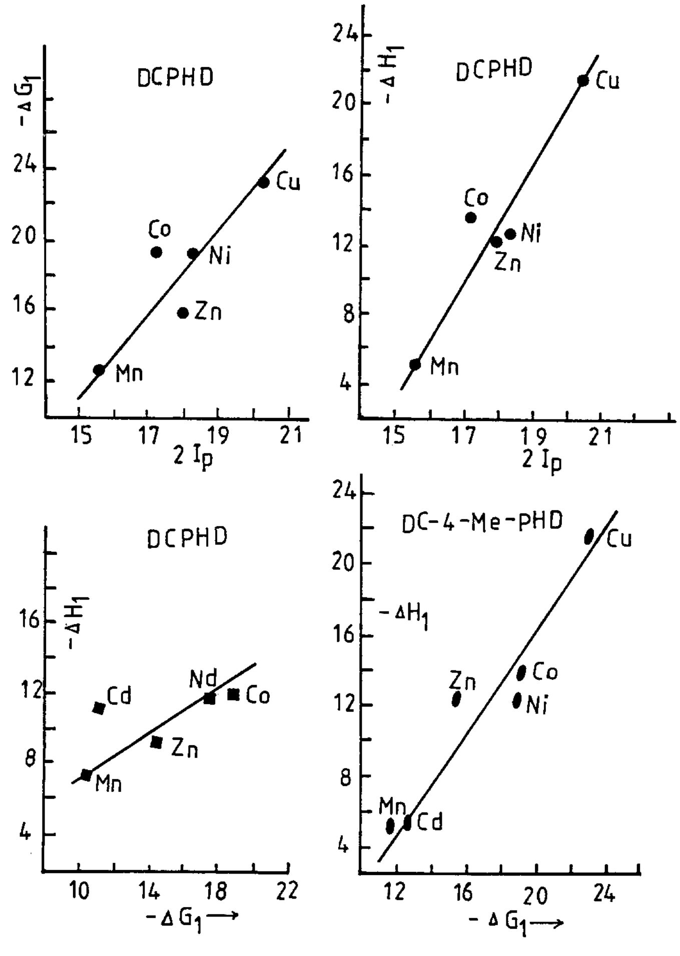

Fig. 2. Correlation between ΔG/ΔH/second ionization potential ($2Ip$) for the chelates of *DCPHD* and *DC-4-Me-PHD*

Table 1. Stability constants of metal chelates of *DCPHD*, *DC*-4-Cl-*PHD* and *DC*-4-*Me*-*PHD* at different temperatures ($\mu = 0.10$, 75% methanol-water)

Cation	*DCPHD*			*DC*-4-Cl-*PHD*			*DC*-4-*Me*-*PHD*		
	$\log K_1$			$\log K_1$			$\log K_1$		
	10 °C	20 °C	30 °C	10 °C	20 °C	30 °C	10 °C	20 °C	30 °C
H^+	8.89±0.01	8.61±0.02	8.46±0.03	8.25±0.01	8.04±0.02	7.88±0.01	9.02±0.02	8.82±0.02	8.83±0.03
Cu^{2+}	17.83±0.05	17.25±0.02	16.71±0.30	17.19±0.30	16.89±0.20	16.49±0.30	17.92±0.02	17.62±0.02	17.30±0.02
Ni^{2+}	14.43±0.03	14.11±0.03	13.78±0.03	13.26±0.04	13.11±0.03	13.03±0.11	13.44±0.07	13.12±0.01	12.82±0.01
Co^{2+}	14.57±0.06	14.22±0.02	13.86±0.08	14.26±0.02	14.15±0.08	14.05±0.01	14.12±0.01	13.80±0.09	13.48±0.03
Zn^{2+}	11.99±0.01	11.66±0.03	11.36±0.03	11.44±0.08	11.24±0.01	11.07±0.01	11.01±0.01	10.72±0.01	10.54±0.03
Mn^{2+}	9.21±0.02	9.08±0.03	8.95±0.01	8.66±0.02	8.42±0.03	8.27±0.01	7.92±0.01	7.68±0.02	7.52±0.01
Cd^{2+}	9.42±0.01	9.29±0.09	9.16±0.01	9.02±0.04	8.80±0.20	8.48±0.01	8.71±0.05	8.39±0.06	8.13±0.05
Fe^{3+}				16.96±0.05	16.51±0.14	16.01±0.10			
UO_2^{2+}				15.68±0.02	15.48±0.08	15.36±0.08	15.50±0.02	15.29±0.02	15.08±0.09
Th^{4+}				16.62±0.10	16.20±0.10	15.98±0.01	15.47±0.02	15.77±0.02	16.05±0.02
Sm^{3+}	10.78±0.02	10.50±0.01	10.25±0.01				10.48±0.01	10.28±0.04	10.18±0.02
	$\log K_2$			$\log K_2$			$\log K_2$		
	10 °C	20 °C	30 °C	10 °C	20 °C	30 °C	10 °C	20 °C	30 °C
H^+				10.28±0.10	10.89±0.09	10.62±0.09	11.30±0.13	10.87±0.05	10.44±0.03
Cu^{2+}	6.70±0.04	6.15±0.10	5.55±0.06						
Ni^{2+}	9.99±0.01	9.49±0.05	8.98±0.09	9.09±0.09	8.98±0.04	8.91±0.01	8.56±0.01	8.16±0.01	7.75±0.01
Zn^{2+}	8.03±0.04	7.80±0.03	7.57±0.03	7.10±0.02	6.89±0.02	6.65±0.03	6.57±0.07	5.84±0.03	5.46±0.04
Mn^{2+}	7.25±0.01	7.12±0.01	6.99±0.01	6.42±0.06	6.07±0.12	5.57±0.06	5.21±0.09	4.71±0.05	4.41±0.01
Cd^{2+}	7.39±0.01	7.31±0.07	7.22±0.01	6.76±0.05	6.59±0.04	6.33±0.01	5.77±0.01	5.42±0.06	4.97±0.02
Fe^{3+}				15.10±0.10	14.95±0.08	14.80±0.08	15.67±0.09	15.35±0.02	14.90±0.02
UO_2^{2+}				14.46±0.10	14.31±0.10	14.26±0.10	11.67±0.22	11.87±0.22	12.06±0.24
Th^{4+}				15.20±0.09	14.92±0.09	14.65±0.8	15.04±0.10	15.31±0.20	15.58±0.20
Sm^{3+}	8.36±0.11	8.00±0.16	7.72±0.08				8.17±0.08	7.98±0.08	7.95±0.08

Table 2. Thermodynamic data for the formation of *DCPHD*, *DC*-4-Cl-*PHD* and *DC*-4-*Me*-*PHD* metal chelates ($\mu = 0.10$, 75% methanol-water; ΔG and ΔH in kcal/mol, ΔS in cal/mol deg)

Cation	*DCPHD*			*DC*-4-Cl-*PHD*			*DC*-4-*Me*-*PHD*		
	$-\Delta G_1$	$-\Delta H_1$	ΔS_1	$-\Delta G_1$	$-\Delta H_1$	ΔS_1	$-\Delta G_1$	$-\Delta H_1$	ΔS_1
H^+	11.74	8.72±0.05	10.0±0.06	10.93	7.26±0.01	12.1±0.02	11.97	7.64±0.01	14.3±0.01
Cu^{2+}	23.18	21.85±0.01	4.4±0.01	22.88	13.69±0.07	30.3±0.16	24.00	12.14±0.01	39.1±0.01
Ni^{2+}	19.12	12.73±0.01	2.1±0.01	18.08	4.52±0.05	44.8±0.53	17.79	12.15±0.01	18.6±0.01
Co^{2+}	19.23	13.90±0.01	17.6±0.01	19.50	4.12±0.01	50.8±0.01	18.70	12.54±0.01	20.3±0.01
Zn^{2+}	15.76	12.34±0.01	11.3±0.01	15.36	7.25±0.01	26.8±0.01	14.62	9.23±0.06	17.8±0.12
Mn^{2+}	12.14	5.09±0.01	24.2±0.01	11.47	7.66±0.05	12.6±0.08	10.43	7.85±0.04	8.5±0.04
Cd^{2+}	12.71	5.00±0.01	25.5±0.01	11.77	10.55±0.08	4.0±0.03	11.28	11.37±0.01	−0.3±0.01
Fe^{3+}				22.21	18.60±0.02	11.9±0.01			
UO_2^{2+}				22.17	6.29±0.05	49.6±0.38	20.92	8.23±0.01	41.9±0.01
Th^{4+}				21.31	12.58±0.16	31.7±0.40	22.27	−11.56±0.01	111.7±0.01
Sm^{3+}	14.22	11.15±0.05	10.1±0.01				19.60	5.90±0.01	45.2±0.02
	$-\Delta G_2$	$-\Delta H_2$	$-\Delta S_2$	$-\Delta G_2$	$-\Delta H_2$	$-\Delta S_2$	$-\Delta G_2$	$-\Delta H_2$	$-\Delta S_2$
H^+	14.94	21.37±0.33	−21.2±0.33	14.73	12.95±0.05	−5.9±0.02	14.49	16.84±0.01	7.8±0.01
Cu^{2+}	7.70	22.51±0.02	48.9±0.05						
Ni^{2+}	12.46	19.78±0.02	24.2±0.02	12.36	3.53±0.02	−29.1±0.17	10.75	15.86±0.01	16.9±0.01
Zn^{2+}	10.50	9.01±0.01	−4.9±0.01	9.23	8.81±0.02	−1.4±0.01	7.58	21.82±0.28	47.0±0.60
Cd^{2+}	10.02	3.33±0.01	−22.1±0.03	8.78	8.40±0.10	1.3±0.05	6.90	15.65±0.10	28.9±0.12
Fe^{3+}				20.53	5.88±0.01	−48.4±0.01	20.67	15.05±0.10	−18.6±0.12
UO_2^{2+}				19.78	3.94±0.01	−52.3±0.02	16.73	−7.64±0.01	−80.4±0.10
Th^{4+}				20.33	10.77±0.01	−31.6±0.01	21.62	−10.58±0.01	−106.3±0.10
Sm^{3+}	10.71	12.02±0.02	4.3±0.01				11.03	8.02±0.01	−9.09±0.01

Table 3. Stability constants of metal chelates of *DCPHD* at different temperatures ($\mu = 0.10$, 75% methanol-water)

Ln^{3+}	$\log K_1$				$log\, K_2$			
	10 °C	20 °C	30 °C	37 °C	10 °C	20 °C	30 °C	37 °C
H^+	8.89 ± 0.01	8.61 ± 0.02	8.46 ± 0.03	8.28 ± 0.02	11.80 ± 0.11	11.04 ± 0.07	10.77 ± 0.05	10.27 ± 0.05
La	9.41 ± 0.02	9.12 ± 0.01	8.95 ± 0.02	8.71 ± 0.09	5.61 ± 0.14	5.26 ± 0.11	4.89 ± 0.11	4.40 ± 0.05
Pr	10.36 ± 0.02	10.01 ± 0.01	9.86 ± 0.01	9.62 ± 0.01	7.53 ± 0.14	6.93 ± 0.04	6.28 ± 0.10	5.95 ± 0.05
Nd	10.52 ± 0.04	10.22 ± 0.01	10.10 ± 0.04	9.83 ± 0.04	8.27 ± 0.13	7.80 ± 0.06	7.50 ± 0.08	7.27 ± 0.11
Sm	10.78 ± 0.02	10.50 ± 0.01	10.25 ± 0.01	9.99 ± 0.17	8.36 ± 0.11	8.00 ± 0.16	7.72 ± 0.08	7.55 ± 0.03
Eu	11.00 ± 0.01	10.71 ± 0.01	10.45 ± 0.01	10.25 ± 0.01	8.85 ± 0.04	8.35 ± 0.14	7.87 ± 0.15	7.60 ± 0.05
Gd	11.07 ± 0.01	10.91 ± 0.01	10.66 ± 0.09	10.40 ± 0.01	8.20 ± 0.06	7.87 ± 0.10	7.43 ± 0.13	7.26 ± 0.12
Tb	11.41 ± 0.01	11.25 ± 0.01	11.07 ± 0.01	10.72 ± 0.01	8.64 ± 0.05	8.21 ± 0.14	7.70 ± 0.16	7.47 ± 0.07
Dy	11.76 ± 0.01	11.51 ± 0.01	11.34 ± 0.03	10.95 ± 0.01	8.98 ± 0.07	8.66 ± 0.12	8.33 ± 0.12	8.03 ± 0.10
Ho	12.00 ± 0.01	11.65 ± 0.02	11.49 ± 0.01	11.04 ± 0.01	8.60 ± 0.14	8.09 ± 0.13	7.57 ± 0.12	7.35 ± 0.11
Er	12.10 ± 0.01	11.72 ± 0.02	11.49 ± 0.01	11.12 ± 0.01	8.50 ± 0.11	8.20 ± 0.16	7.57 ± 0.11	7.22 ± 0.03
Tm	12.45 ± 0.01	12.15 ± 0.01	11.86 ± 0.01	11.50 ± 0.01	9.81 ± 0.04	9.33 ± 0.03	8.98 ± 0.12	8.55 ± 0.12
Yb	12.44 ± 0.01	11.96 ± 0.01	11.82 ± 0.02	11.57 ± 0.04	8.76 ± 0.16	8.21 ± 0.03	7.93 ± 0.11	7.74 ± 0.11
Lu	12.44 ± 0.01	12.07 ± 0.01	11.85 ± 0.01	11.61 ± 0.01	9.75 ± 0.06	9.22 ± 0.05	9.10 ± 0.08	8.58 ± 0.12

this relation is used it is implicitly assumed that only bond strength or ΔH is involved. Since the second ionization potential may be taken as a rough estimation of the average electron attracting power of a divalent metal ion it will also be a measure of the attracting power of that divalent metal ion for a source of electrons such as found in the chelate groups. Hence it is more nearly related to bond energy and ΔH of chelation than to ΔG as measured by the log of the chelate formation constant. It is also to be noted that ΔH should be a more sensitive index of bond strength than ΔG. Figure 2 shows a plot of $2Ip$ of the gaseous metal atom against ΔH and ΔG of chelation. As can be seen the relationship is satisfactory.

A comparison of ΔH values listed in Table 2 points out the importance of steric hindrance in all chelates of *DC-4-Me-PHD*. In all cases the heats of chelation (ΔH_1) for *DC-4-Me-PHD* are less negative than that found for *DCPHD*, with exception of the Mn(II) and Cd(II) chelates. For the (ΔH_2) the order is reversed, i.e. *DCPHD* chelates are less exothermic than the chelates of *DC*-4-*Me-PHD* (Table 2). In general, the less exothermic values of ΔH indicate a decrease in bond strength due to the hindrance of the methyl group. However, the basicity of the ligands cannot be ignored. This could be illustrated by the comparison of thermodynamic parameters of metal chelates of both *DCPHD* and *DC*-4-Cl-*PHD*. The order of ΔH_1 and ΔG_1 is as follows; *DCPHD* > *DC*-4-Cl-*PHD* which is the same order of the basicity $\Sigma(PK_1^H + pK_2^H)$ of the ligands.

The higher negative enthalpy and positive entropy obtained for the most of the complex systems (Tables 2 and 4) indicate that the complex species is stable and favored in 75% (*v*/*v*) methanol-water. The enthalpy change associated with the complexation reaction is a measure of the difference in bond energy toward the metal ion between the ligand and the coordinated molecule of solvent. Thus, the higher negative enthalpy of most of the present complex systems indicates the poor coordinating ability of methanol-water as solvent.

Table 4. Thermodynamic data for the formation of *DCPHD* complexes of lanthanide(III) ions ($\mu = 0.10$, 75% methanol-water; ΔG and ΔH in kcal/mol, ΔS in cal/mol deg)

Ln^{3+}	$-\Delta G_1$	$-\Delta H_1$	ΔS_1	$-\Delta G_2$	$-\Delta H_2$	$-\Delta S_2$
H^+	11.74	8.72 ± 0.05	10.0 ± 0.06	14.94	21.37 ± 0.33	−21.2 ± 0.33
La	12.61	9.93 ± 0.08	8.9 ± 0.08	6.78	17.31 ± 0.30	34.8 ± 0.60
Pr	13.68	10.41 ± 0.12	10.8 ± 0.12	8.71	23.83 ± 0.02	49.9 ± 0.04
Nd	14.01	9.55 ± 0.17	14.7 ± 0.27	10.40	14.62 ± 0.05	13.9 ± 0.05
Sm	14.22	11.15 ± 0.05	10.1 ± 0.01	10.71	12.02 ± 0.02	4.3 ± 0.01
Eu	14.50	11.05 ± 0.07	11.4 ± 0.01	10.92	18.71 ± 0.01	25.7 ± 0.01
Gd	14.79	9.78 ± 0.19	16.5 ± 0.32	10.31	14.43 ± 0.06	13.6 ± 0.05
Tb	15.36	9.62 ± 0.43	18.9 ± 0.85	10.68	17.79 ± 0.03	23.5 ± 0.05
Dy	15.37	11.42 ± 0.39	13.0 ± 0.44	11.56	13.90 ± 0.05	7.7 ± 0.03
Ho	15.94	13.10 ± 0.40	9.4 ± 0.30	10.50	18.95 ± 0.04	27.9 ± 0.06
Er	15.94	13.81 ± 0.20	7.0 ± 0.10	10.50	19.54 ± 0.26	29.8 ± 0.40
Tm	16.45	13.64 ± 0.16	9.3 ± 0.11	12.46	18.05 ± 0.10	18.4 ± 0.11
Yb	16.40	12.00 ± 0.43	14.5 ± 0.53	11.00	14.90 ± 0.19	12.9 ± 0.16
Lu	16.44	11.93 ± 0.06	14.9 ± 0.08	12.62	15.75 ± 0.55	10.3 ± 0.36

The complex formation in mixed organic-water solvent is best explained by considering the nature of forces in separate solvents (i.e. methanol and water) and mixed solvents (methanol-water). In a solvent S the solvation reaction can be written as:

$$Ln^{3+}_{(g)} + nS_{(1)} \overset{K_s}{\longleftrightarrow} LnS^{3+}_{n(1)} \tag{1}$$

where $Ln^{3+}_{(g)}$ is the free lanthanide ion in vacuo, $LnS^{3+}_{n(1)}$ the solvated ion in the liquid solvent and K_s the solvation equilibrium constant. The free energy of transfer of the cation from solvent A to solvent B (ΔG_{tr}) is the difference in the standard free energy changes for the solvation equilibria in the two solvents. Thus, for

$$LnA^{3+}_{n} + mB \longleftrightarrow LnB^{3+}_{m} + nA \tag{2}$$

we have

$$\Delta G_{tr} = -RT \ln B \tag{3}$$

$$B = K_B/K_A. \tag{4}$$

For mixed solvation

$$LnA^{3+}_{n} + iB \overset{K_i}{\longleftrightarrow} LnA_{n-i}B^{3+}_{i} + iA,$$

the free energy of transfer from A to any mixture of A and B is given by [5]:

$$\Delta G_{tr} = -nRT \ln \varphi_A - RT\left\{1 + \sum_{i=1}^{n} \left(\frac{\varphi_B}{\varphi_A}\right)^{i}\right\} \tag{5}$$

where φ_A and φ_B are the volume fractions of A and B, respectively.

The behavior of mixed solvents can be discussed in terms of two limiting cases in which one solvent acts as a better donor than the other [6]. First, consider B to be the better donor i.e. $\beta_i \gg 1$. In this case, addition of small amounts of B results in a rapid increase of solvent B in the first hydration sphere with reference to the bulk solvent. This increase is continued until a constant maximum value is reached for which the concentration of B is sufficient to solvate the lanthanide ion completely. An example of this case is the solvation of Eu^{3+} in water-*DMSO* mixture.

In the second case, consider A to be the better donor, i.e. $\beta_i \ll 1$. In this case, addition of B to A results in the dilution of solvent A and the value of B in the first hydration sphere increases more slowly than the increase in mole fraction of B in the solvent mixture. This is the case of Eu^{3+} solvation [7] by mixtures of water-methanol, water-acetone, water-acetonitrile, and water-1,4-dioxane. A less regular behavior can be expected for systems in which strong interactions exist between solvent molecules A and B or between coordinated and bulk solvent molecules as well as for those in which the steric barrier increases markedly with the degree of solvation. Such an irregular pattern is observed in the solvation of Eu^{3+} in a water-*DMF* mixture.

On the basis of reference reports [8–10] and the second state given above, it has been found that the methanol molecules take part in the solvation of lanthanide ions. With the increase of the methanol concentration (i.e. 75% methanol-water) of the solvent mixture, the water molecules can be replaced by alcohol molecules. This

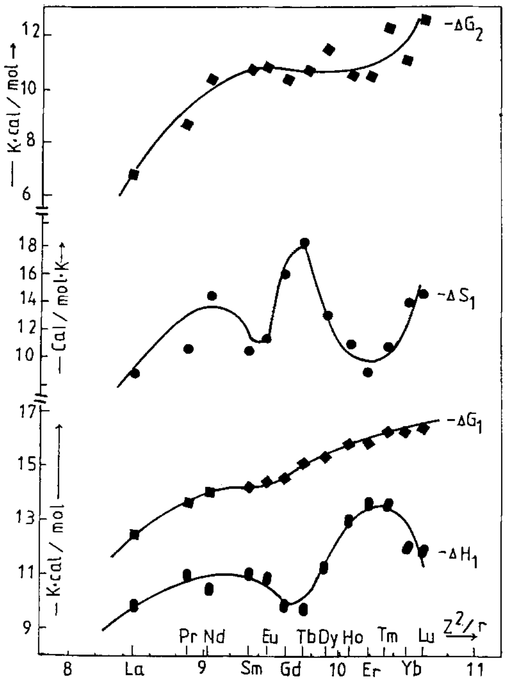

Fig. 3. Thermodynamic parameters in complexation between lanthanoid(III) and *DCPHD*

will cause: (a) steric crowding within the inner solvation shell, and (b) change of dielectric constant of the medium. Both (a) and (b) tend to cause enhancement in the complexing ability of ligand anion in 75% (*v*/*v*) methanol-water compared to water solvent. The higher negative values of ethalpy (ΔH_1 or ΔH_2) for heavier lanthanides compared to that of lighter ones could be taken as a good evidence for the crowding approach given above. The heavy lanthanide ions solvation would be expected to be more sensitive to crowding than the lighter ions because of relative cationic radii [11].

The values of the entropy change for the second step of the complex formation (ΔS_2) are much less than those for the first step, ΔS_1. This variation in entropy can be attributed to: (1) the purely statistical effect, and (2) the fact that the first step of complex formation causes the removal of the highly charge M^{n+} ion from the solution, thus resulting in a greater increase in entropy than the second step, which does not involve such a highly charged ion (i.e. *ML*).

The positive entropy change (ΔS_1) upon complexation is a composite of: (a) a negative contribution due to the conversion of translational entropy of the free ligand, (b) a positive entropy due to release of coordinated solvent molecules, and (c) a decrease in entropy of translation by the formation of one chelate from two species.

For reactions between doubly charged donor groups (L^{2-}) and M^{2+} or M^{3+} ions, the entropy change associated with (b) predominates because of neutralization of charges on metal ions.

In Fig. 3, the patterns of the variation with lanthanide ionic potentials (Z^2/r) are similar for different ligands. All curves can be resolved in an initial group (the lighter lanthanides) an intermediate group (Sm-Dy) and a final group (the heavier ones).

The trends observed in the enthalpy changes as a function of ionic potentials may be explained in terms of different hydration number of the lighter and the heavier lanthanide ions [12].

The variation of entropy with ionic potential shown in Fig. 3, was also consistent with the model of considering different hydration numbers for lighter and heavier lanthanide ions. In order to substantiate this model we refer to the ligational entropy change for the lanthanide metal ion. Thus, for the reaction:

$$Ln^{3+}(aq) + X^{2-} \rightleftharpoons LnX^{+}$$

$$\Delta S = S_{LnX} - S_{Ln^{3+}} - S_{X^{2-}}$$

and

$$(\Delta S + S_{Ln^{3+}}) = S_{LnX} - S_{X^{2-}} \tag{6}$$

where S terms represent the standard partial molal entropies of the species LnX, Ln^{3+} and X^{2-} in aqueous solution (X^{2-} = ligand anion). Unfortunately, available data for $S_{Ln^{3+}}$ [13] were known in water only. The similarities of the rate constant (K in S^{-1}) values for the exchange of water in water [14] and water-methanol [15] suggests the use of $S_{Ln^{3+}}$ in water for 75% (v/v) methanol-water medium.

For a series of lanthanide-*DCPHD* systems the left hand side of Eq. (6) provides a relative measure of S_{LnX}, since the term $S_{X^{2-}}$ is common. Table 5 summarizes the results of these calculations. It can be seen that the relative entropy of the complex ion LnX^{-} (as expressed by the quantity "$\Delta S + S_{Ln^{3+}}$") is essentially constant for the lanthanides La to Gd (26.9 ± 2.3 cal/mol deg). The second group from Tb to Lu has constant values of 34.6 ± 2.9 cal/mol deg. The difference between the two groups is 7.4 cal/mol deg.

The concentration of water in dilute aqueous solution is equal to 55.0 mol/l. Thus, for a dehydration reaction

$$M(\mathrm{H_2O})_n^{m+}(a) \rightleftharpoons M^{M+}(a) + n\mathrm{H_2O}(a)$$

$$\Delta S_{cratic} = nR \ln 55. \tag{7}$$

ΔS_{cratic} for a process involving dehydration of one molecule of water from the coordination sphere of metal ion is $R \ln 55 = 8.0$ cal/mol deg.

Table 5. Relative partial molal entropy (in cal/mol deg) of *Ln*(III)-*DCPHD* complexes

Ln^{3+}	$S_{Ln^{3+}}$	$\Delta S + S_{Ln^{3+}}$	Ln^{3+}	$S_{Ln^{3+}}$	$\Delta S + S_{Ln^{3+}}$
La	−34.7	−25.8	Tb	−42.7	−23.8
Pr	−37.5	−26.7	Dy	−43.6	−30.6
Nd	−38.5	−23.8	Ho	−44.5	−35.1
Sm	−40.3	−30.2	Er	−45.3	−38.3
Eu	−41.1	−29.7	Tm	−46.1	−36.8
Gd	−41.8	−25.3	Yb	−46.8	−32.3
			Lu	−47.5	−32.6
Mean = 26.9 ± 2.3 cal/mol deg				34.3 ± 2.7 cal/mol deg	
Difference = 7.4 cal/mol deg					

Spedding et al. [12] proposed that the difference in hydration numbers between light and heavy lanthanide ions seems not to exceed unity and suggested that the probable species for the light cations is $Ln(H_2O)_9^{3+}$ and for the heavy ones $Ln(H_2O)_8^{3+}$. The difference 7.4 cal/mol deg for the entropy of light and heavy lanthanide elements is equivalent to the dehydration of one molecule of water from the coordination sphere of the metal ion; this value is in good agreement with the obtained using Eq. (7).

The comparison between ΔH_1 for Sm(III)-*DCPHD* and Sm(III)-*DC*-4-*Me*-*PHD* complexes shows that the former is more exothermic (Table 2). The difference in ΔH_1 between *DCPHD* and *DC*-4-*Me*-*PHD* could be related to the difference in the dehydration of the ligands when they are complexed, since the difference in ΔH_1 is about the same as for the protonation heat, e.g. the difference in $\Sigma(\Delta H_1 + \Delta H_2)$ of protonation for the two ligands equals 5.61 kcal/mol and that of ΔH_1 for samarium(III) is 5.25 kcal/mol.

A comparison between the relative stability of corresponding complexes of Th^{4+} and UO_2^{2+} ions show that the higher stability of thorium complexes is due to a larger gain in entropy (Table 2). The more positive values of ΔH_1 and ΔS_1 for the formation of Th^{4+}-*DC*-4-*Me*-*PHD* complexes compared to those of uranyl ion probably reflect the difference in charge between the two metal ions. In fact, the highest charged ion has a larger and more ordered hydration sphere, as a consequence in complexation reactions this involves a higher favorable entropy term and an extra dehydration energy, only in part supplied by the stronger electrostatic interactions.

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