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THERMODYNAMIC STUDIES OF THE COMPLEXATION REACTION INVOLVING TRIVALENT METAL IONS AND BENZIL-4-METHYL-2-QUINOLYLHYDRAZONE (BMQH)

B.S. GARG *, MANJU PAL and RANJANA DIXIT

Department of Chemistry, University of Delhi, Delhi 110007 (India)

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ABSTRACT

The stepwise stability constants of 1:1, 2:1 and 3:1 complexes of benzil-4-methyl-2-quinolylhydrazone (BMQH) with lanthanons(III) have been determined pH-metrically in a 75% (v/v) ethanol–water medium at various temperatures and ionic strengths. Values of $\bar{n}$ and pL have been found by Bjerrum and Calvin's method, as modified by Irving and Rossotti. The stability constants and the values of S_{min} have been calculated. The order of stability constants has been found to be La(III) < Pr(III) < Gd(III) < Nd(III) < Sm(III) < Tb(III) < Dy(III) < Ho(III).

The thermodynamic parameters ΔG, ΔH and ΔS have also been calculated, and the effect of varying dielectric constant of the medium on stabilities has been investigated, at $30 \pm 0.5\,^\circ$C and $\mu = 0.1$ M NaCl.

INTRODUCTION

Hydrazones are well known for their analytical and biological applications. They are used as plasticizers, stabilizers for polymers, antioxidants, etc. Hydrazones can act as herbicides, insecticides, nematocides, rodenticides and plant growth regulators. Substituted hydrazones have been found to exhibit spasmolytic activity, hypotensive action and activity against leukaemia [1]. Many of the physiologically active compounds find application [2] in the treatment of diseases such as tuberculosis, leprosy and mental disorder. A literature survey revealed that no work has been done on the lanthanon complexes of benzil-4-methyl-2-quinolylhydrazone (BMQH). So the present study was undertaken to determine the stability constants of complexes of lanthanons with BMQH at various ionic strengths and temperatures and in various aquo-organic mixtures.

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* Author to whom all correspondence should be directed.

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EXPERIMENTAL

A digital pH meter (ECIL model PH-5651) in conjunction with a glass electrode was used for pH measurements. The pH meter was standardized with potassium hydrogenphthalate buffer before the titration was performed.

Benzil (0.1 mol, 1.26 g) was dissolved in ethanol to give a saturated solution. A saturated solution of 2-hydrazinolepidine (0.1 mol, 1.73 g) in the minimum volume of concentrated HCl was added and the mixture was refluxed for one hour. After completion of the reaction the mixture was cooled and filtered to give a yellow coloured final product which was recrystallized from ethanol. The purity of the product was checked by NMR, elemental analysis and thin layer chromatography (m.p. 220 ° C).

Metal ion solutions were prepared from AnalaR lanthanon nitrate samples (Indian Rare Earth Ltd.). Ligand solution was prepared in freshly distilled ethanol. NaCl (Riedel) was used to maintain constant ionic strength. A solution of sodium hydroxide (NaOH) Merck) in 75% aqueous ethanol was used as the titrant, and was standardized with oxalic acid. All other chemicals used were of reagent grade. The titrations were carried out in a nitrogen atmosphere, which was presaturated with 75% (v/v) aqueous ethanol. Ethanol was purified by the method given by Vogel [3].

Bjerrum and Calvin's method, as modified by Irving and Rossotti [4], was used to determine $\bar{n}$ and pL values. The following solutions were titrated potentiometrically against standard 0.05 M NaOH in 75% (v/v) ethanol–H_2O to determine $\bar{n}$ and pL values for the formation of the complexes

(i) 1.5 ml HCl (0.05 M) + 2 ml NaCl (2.0 M) + 0.5 ml K_2SO_4 or KNO_3 (0.01 M) + 1.0 ml H_2O + 15.0 ml ethanol

(ii) 1.5 ml HCl (0.05 M) + 2 ml NaCl (2.0 M) + 0.5 ml K_2SO_4 or KNO_3 (0.01 M) + 0.5 ml H_2O + 15.0 ml ligand in ethanol (0.005 M)

(iii) 1.5 ml HCl (0.05 M) + 2.0 ml NaCl (2.0 M) + 0.5 ml metal sulphate or nitrate (0.01 M) + 10.0 ml ligand (0.005 M) + 5.0 ml ethanol.

These titrations were repeated for ionic strengths of $\mu = 0.02$, 0.05 and 0.2 M NaCl, and for temperatures of 30, 40 and 50 ° C. Values of $\bar{n}$ and pL were computed from the titration curves of solutions (i), (ii) and (iii), using an Uptron PC computer.

The corresponding values of stability constants were calculated using the weighted least-squares method of Sullivan et al. [5]. The weighted least-squares treatment determines that set of β_n which makes the function

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

nearest to zero, by minimizing

$$S,\ S = \sum_{i=1}^{I} W_i U^2(x_i y_i z_i)$$

with respect to the variation in β_n. We report the $S_{\min}$ values for various metal complexes. $S_{\min}$ has the same statistical distribution as χ^2 with K degrees of freedom and weights defined in accordance with Rydberg and

TABLE 1

Stability constants of lanthanon complexes of BMQH at various ionic strengths (μ) and temperatures (T) in a 75% (v/v) ethanol–water medium

System	Constant	Conditions					
		$\mu =$ 0.02	0.05	0.1	0.1	0.1	0.2
		$T =$ 30	30	30	40	50	30
Ligand	pK_a	5.50	5.32	4.76	4.66	4.40	4.52
Ho(III)–BMQH	log K_1	4.644	4.359	4.027	3.646	3.677	3.591
	log K_2	3.443	3.648	3.749	3.139	3.276	2.995
	log K_3	2.643	2.315	2.148	2.611	1.728	2.343
	$S_{\min}$	0.0057	0.0130	0.0156	0.0170	0.0015	0.0430
Dy(III)–BMQH	log K_1	4.571	4.299	3.771	3.614	3.573	3.516
	log K_2	3.631	3.545	3.929	2.939	3.232	2.934
	log K_3	2.039	2.061	1.980	2.539	0.752	2.246
	$S_{\min}$	0.0008	0.0021	0.0012	0.017	0.0012	0.0120
Tb(III)–BMQH	log K_1	4.516	4.242	3.715	3.609	3.554	3.481
	log K_2	3.309	3.390	3.641	2.832	3.077	2.741
	log K_3	1.689	1.993	1.913	2.185	–	2.116
	$S_{\min}$	0.0085	0.0011	0.0076	0.0031	0.0038	0.0028
Sm(III)–BMQH	log K_1	4.420	4.214	3.646	3.628	3.467	3.478
	log K_2	3.149	2.926	3.462	2.641	2.925	2.552
	log K_3	1.504	1.880	1.798	1.906	–	1.901
	$S_{\min}$	0.0002	0.0008	0.0032	0.0006	0.0069	0.0005
Nd(III)–BMQH	log K_1	4.282	4.231	3.582	3.589	3.486	3.420
	log K_2	2.785	3.015	2.861	2.586	2.690	2.502
	log K_3	1.144	1.417	1.543	1.193	–	0.721
	$S_{\min}$	0.0003	0.0025	0.0009	0.0002	0.0020	0.0001
Gd(III)–BMQH	log K_1	4.131	4.070	3.535	3.546	3.446	3.376
	log K_2	2.543	2.903	2.596	2.368	2.425	2.367
	log K_3	1.108	1.261	1.317	1.239	–	–
	$S_{\min}$	0.0010	0.0010	0.0008	0.0003	0.0017	0.0001
Pr(III)–BMQH	log K_1	3.969	3.931	3.458	3.464	3.358	3.236
	log K_2	2.329	2.678	2.391	2.180	2.071	2.155
	log K_3	1.354	1.213	1.291	0.876	–	–
	$S_{\min}$	0.0013	0.0004	0.0013	0.0006	0.0023	0.0000
La(III)–BMQH	log K_1	3.758	3.435	3.398	3.349	3.296	3.037
	log K_2	1.783	2.291	2.138	1.989	1.839	2.014
	log K_3	(negative)	1.182	1.045	0.517	–	–
	$S_{\min}$	0.0071	0.0000	0.0002	0.0001	0.0010	0.0001

Sullivan [6]. S_{min} can be equated to χ^2. ΔH was calculated by the graphical method of Yatsimirskii and Vasil'ev [7]; ΔG and ΔS were calculated by conventional methods.

RESULTS AND DISCUSSION

Order of stability constants

The stability constants of the metal complexes of BMQH were found to increase from lanthanum(III) to holmium(III) with increasing Lewis acidity of the metal ion. The order of log K_1 values for BMQH–Ln complexes was found to be: La(III) < Pr(III) < Gd(III) < Nd(III) < Sm(III) < Tb(III) < Dy(III) < Ho(III).

The value for Gd(III) is lower than that for Nd(III), the familiar 'gadolinium break' [8].

Effect of ionic strength and temperature

In the present investigation it was observed that the value of the dissociation constant pK of the ligand decreases with increasing ionic strength of the medium (Table 1), which is in agreement with the Debye–Hückel equation [9]. A similar trend of variation was observed for the stability constants of the complexes (Table 1).

The values of the stability constants and of pK_a in Table 1 reveal that the stability constants decrease steadily with increasing temperature. The overall free energy, enthalpy and entropy changes at 30 ± 0.5 °C are reported in

TABLE 2

Thermodynamic parameters of lanthanon complexes with BLH at $\mu = 0.1$ M NaCl and $T = 30 \pm 0.5°$

Metal ion	$-\Delta G$ (kJ mol^{-1})	$-\Delta H$ (kJ mol^{-1})	ΔS (kJ mol^{-1} K^{-1})
Ho(III)	22.969	23.358	0.00128
Dy(III)	20.417	21.873	0.00615
Tb(III)	17.866	21.547	0.01213
Sm(III)	15.314	21.145	0.01924
Nd(III)	12.762	20.777	0.02635
Gd(III)	10.211	20.501	0.00339
Pr(III)	7.655	20.057	0.04099
La(III)	5.103	19.706	0.04810

Table 2. The results indicate that ΔG and ΔH are negative, which shows that complexation reactions are favourable at ordinary temperatures. The positive ΔS values show that the system is entropy stabilized.

TABLE 3

Stability constants of lanthanon complexes of BMQH in various aquo-organic mixtures at $\mu = 0.1$ M NaCl and $T = 30 \pm 0.5\,^\circ$C

System	Constants	Aquo-organic mixtures				
		50% ethanol–H_2O	60% ethanol–H_2O	75% ethanol–H_2O	75% acetone–H_2O	75% dioxan–H_2O
Ligand	pK_a	4.35	4.62	4.76	5.28	5.60
Ho(III)–BMQH	log K_1	3.698	3.784	4.027	4.383	4.688
	log K_2	3.582	3.645	3.749	3.597	3.766
	log K_3	1.758	1.849	2.148	2.062	2.498
	S_{min}	0.0030	0.0180	0.0156	0.0094	0.0093
Dy(III)–BMQH	log K_1	3.538	3.634	3.771	4.394	4.644
	log K_2	3.435	3.543	3.929	3.375	3.651
	log K_3	1.590	1.781	1.980	1.816	
	S_{min}	0.0010	0.0045	0.0012	0.0026	0.0820
Tb(III)–BMQH	log K_1	3.513	3.594	3.715	4.236	4.581
	log K_2	3.199	3.328	3.641	3.297	3.473
	log K_3	1.504	1.831	1.913	1.554	1.550
	S_{min}	0.0014	0.0011	0.0076	0.0027	0.0036
Sm(III)–BMQH	log K_1	3.450	3.581	3.646	4.122	4.498
	log K_2	2.983	3.019	3.462	3.295	3.228
	log K_3	1.282	1.771	1.798	1.883	1.807
	S_{min}	0.0029	0.0007	0.0032	0.0020	0.0043
Nd(III)–BMQH	log K_1	3.342	3.579	3.582	4.167	4.439
	log K_2	2.802	2.675	2.861	2.768	3.009
	log K_3	0.235	1.762	1.543	0.958	1.738
	S_{min}	0.0013	0.0003	0.0009	0.0004	0.0018
Gd(III)–BMQH	log K_1	3.399	3.534	3.535	4.142	4.291
	log K_2	2.528	2.436	2.596	2.541	2.789
	log K_3	–	1.316	1.317	0.414	1.198
	S_{min}	0.0023	0.0001	0.0008	0.0005	0.0028
Pr(III)–BMQH	log K_1	3.304	3.432	3.458	4.054	4.155
	log K_2	2.370	2.410	2.391	2.501	2.711
	log K_3	–	1.225	1.291	–	–
	S_{min}	0.0008	0.0002	0.0013	0.0001	0.0037
La(III)–BMQH	log K_1	3.201	3.309	3.398	3.781	4.076
	log K_2	2.189	2.382	2.138	2.334	2.555
	log K_3	–	1.163	1.045	–	–
	S_{min}	0.0003	0.0001	0.0002	0.0004	0.0026

Effect of the dielectric constant

The proton–ligand constants and the formation constants for the metal complexes with BMQH were measured in dioxan–water, acetone–water and ethanol–water media.

The dielectric constant of the media was changed by varying the percentage of the organic component of the medium.

From Table 3, for a given mixed aqueous solvent ethanol–H_2O, 50, 60 and 75% (v/v), it is clear that the pK_a of the ligand increases with increasing organic content of the aquo-organic solvent. This may be due to a decrease in the dielectric constant of the medium, an increase in proton solvation, or a decrease in the hydrogen-bonding ability of the solvent.

The data in Table 3 show that the metal–ligand formation constants increase with increasing percentage of organic solvent in the medium, i.e.

$$\text{ethanol–H}_2\text{O (75\% v/v)} > \text{ethanol–H}_2\text{O (60\% v/v)} > \text{ethanol–H}_2\text{O (50\% v/v)}$$

In general, the stability of complexes containing either an O–H or an O–M link increases with increasing organic content of the solvent [10,11], owing to the decrease in the dielectric constant of the bulk solvents. As the dielectric constant decreases, the ion–ion interaction involving the proton (or metal ion) and the anionic oxygen donor of the ligand increases to a greater extent than does the ion–dipole interaction between the proton (or metal ion) and the solvent molecules.

For a particular composition (75% v/v) of the solvent–water mixture, $1/\epsilon$ values for the various aquo-organic solvents decrease as follows

dioxan–water > acetone–water > ethanol–water

The stability constants for metal complexes with BMQH and pK_a values also follow the same order.

The maximum $\bar{n}$ values observed in the present work were ~ 3.0, which supports our assumption of 1 : 3 stoichiometry. Finally, in view of the very low concentration (5.0×10^{-4} M) of metal ions used in the titration, the possibility of the formation of a polynuclear complex is negligibly small.

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