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THERMODYNAMICS OF THE INTERACTION OF LANTHANUM(III) WITH 1-PHENYL-3-METHYL-4-BENZOYLPYRAZOLONE-5 IN AQUEOUS DIOXANE

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ABSTRACT

The thermodynamics of the interaction between lanthanum(III) with 1-phenyl-3-methyl-4-benzoylpyrazolone-5 (PMBP) have been investigated in 70% (v/v) aqueous dioxane medium at 25 and 35 ± 0.01°C, adopting the Bjerrum–Calvin pH-titration technique, as applied by Van Uitert and Hass. The refinement of the results of formation constants has been accomplished by the method of least squares after an algebraic transformation. The formation of 1 : 1, 1 : 2 and 1 : 3 complexes has been observed, the order of stability being $\log K_1 > \log K_2 > \log K_3$. The changes in ΔG^0, ΔH^0 and ΔS^0 for the complexation reactions have also been evaluated. Factors affecting chelate stability are briefly discussed.

INTRODUCTION

Pyrazolones are prominent analytical reagents [1–5] and potent drugs [6–8]. The importance of these compounds is partly due to their ability to form complexes with a host of metal ions under varied conditions of temperature and acidity. Of these, 1-phenyl-3-methyl-4-benzoylpyrazolone (PMBP) and its substituted analogues have proved to be most useful as potential reagents for the solvent extraction of metals, especially actinide, lanthanide and alkaline earth ions [9–23]. The versatility of PMBP is comparable to the more popular chelating extractant, 2-thenoyltrifluoroacetone (TTA), but surpasses TTA in terms of its relatively much lower cost [24], storage stability and ability to extract most metal ions efficiently from solutions of lower pH [10,12,13]. These considerations led many workers to investigate its coordination with a number of cations [25–27]. No attempt appears to have been made concerning the composition, structure and stability of lanthanum(III) complexes of PMBP in solution. Solid lanthanum chelates have, however, been successfully isolated and characterised very recently [28,29].

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The present paper systematically investigates the interaction of PMBP with lanthanum(III) in 70% (v/v) dioxane–water mixtures at 25 and 35 ± 0.01 °C, following the Bjerrum–Calvin pH-titration technique as modified by Van Uitert and Hass [30] and provides information concerning stoichiometry, stability and associated standard thermodynamic functions. Aqueous dioxane is employed as the solvent medium because of the inadequate water solubility of the reagent as well as its metal chelates. The usefulness of data on metal–ligand stability constants in analytical chemistry arises from its important application in predicting values of solution parameters appropriate for analytical estimations. Also, a detailed knowledge of such equilibrium constants and related standard thermodynamic parameters is essential both in suggesting improvements in separation techniques and in helping to understand the bonding and stereochemistry of complex species.

EXPERIMENTAL

All the chemicals used were of AR (B.D.H.) or GR (Merck) grade. Dioxane was purified following the recommended procedure [31]. PMBP was synthesised following Jensen's method [32] and recrystallised from chloroform to obtain yellow crystals of the enol form (m.p., 92°C; found: C, 73.10; H, 5.10%; calc. for $C_{17}H_{14}N_2O_2$: C, 73.35; H, 5.03%). Lanthanum(III) perchlorate was prepared by the action of concentrated $HClO_4$ with solid La_2O_3. After crystallisation from aqueous acidic solution, the salt was dissolved in 0.01 M $HClO_4$ and the La^{3+} content determined volumetrically with EDTA using xylenol orange as the indicator. An aqueous solution (10%) of tetramethyl ammonium hydroxide (TMAH) titrant was standardised against potassium hydrogen phthalate and diluted to 0.1 M; the proportion of dioxane and water being 70 : 30.

All pH measurements were made with an Orion Research pH meter (model 701A) which can be read to 0.001 pH units.

Titration procedure

A weighed quantity of PMBP, corresponding to a 0.01 M solution in a final volume of 50 ml, was placed on a dry titration vessel to which was added 35 ml of freshly distilled dioxane. Five ml of ~ 0.005 M metal salt solution and 10 ml of 0.01 M $HClO_4$ were then added to give a 70% (v/v) final composition of dioxane–water in the mixture. Due allowance was made for the contraction in volume on mixing the solvents [33,34].

The titration vessel with its contents was then thermostated at 25 or 35 ± 0.01 °C. The glass and calomel electrodes were placed in the titre and titrated by adding small aliquots of TMAH and noting the pH meter reading. Titrations were repeated until two sets of values differing by only

±0.01 pH units were attained. A ratio of 10:1 of the ligand to metal ion concentration was invariably maintained in order to satisfy the highest possible coordination number of the metal ion under investigation. For determining the thermodynamic acid dissociation constant of PMBP, $^{T}\mathrm{p}K_a$, essentially the same procedure was followed without the addition of metal ion solution [35].

CALCULATIONS

Values of the stepwise formation constants K_1, K_2 and K_3 for the La^{3+}–PMBP system were evaluated by least-squares analysis (rejecting the most divergent data especially for the low values of the $\bar{n}$ function) as given by Albert and Serjeant [36]. Procedural details of the calculations are the same as those published elsewhere [37]. Other computational methods, viz. interpolation at half $\bar{n}$ values (Bjerrum's half integral method) as well as point-wise calculation [38], employing the following general equation, were also utilized for log β_n calculations.

$$\log K_n = \mathrm{pL} + \log[\bar{n} - (n-1)/(n-\bar{n})]$$

Compared to these methods, the constants are best evaluated by the least-squares methods, which makes use of all the experimental data incidental to the plot of $\bar{n}/(\bar{n}-1)[\mathrm{L}^-]$ against $(2-\bar{n})[\mathrm{L}^-]/(\bar{n}-1)$ to obtain the intercept, β_1, given by the equation

$$\frac{\bar{n}}{(\bar{n}-1)[\mathrm{L}^-]} = \frac{(2-\bar{n})[\mathrm{L}^-]}{(\bar{n}-1)}\beta_2 - \beta_1$$

Details regarding the calculations of standard thermodynamic functions (ΔG^0, ΔH^0, ΔS^0) and other relevant information have already been published [27].

RESULTS AND DISCUSSION

Figure 1 depicts the metal–ligand formation curves obtained by plotting pL vs. $\bar{n}$ data and does not indicate flattening at the integral values of $\bar{n}$. In all La–PMBP titrations, the $\bar{n}$ values steadily increased with pH from < 0.2 to $1.5 \leqslant 2.5$ before precipitation occurred indicating that 1:3 metal–ligand chelates represented the highest degree of complexation achieved. Values of overall thermodynamic formation constants, $^{T}\log \beta_1$, $^{T}\log \beta_2$ and $^{T}\log \beta_3$, evaluated by the various methods are in good agreement (Table 1) and follow the sequence: $\log K_1 > \log K_2 > \log K_3$. Compared to graphical methods, these computational methods provide greater statistical accuracy and yield true thermodynamic constants at all points. Although the values obtained by the least-squares method would be more acceptable, it may be seen that interpolation at half integral values are also quite representative of the stability constants. The ${}^T\log\,\beta_n$ values are positive and increase on increasing temperature. This shows that higher temperatures favour the formation of complexes. Results of the ${}^Tp K_a$ determination of PMBP have been published elsewhere [35]. Since activity coefficient corrections have been applied, the ${}^T\log\,\beta_n$ values reported here are thermodynamic constants which are reproducible to ± 0.05 log units. Variation in the initial concentration of La^{3+} and PMBP yielded results with a variation of ± 0.10 log units. There was no evidence of metal ion hydrolysis, polynuclear species or protonated complexes.

As normally encountered, the average stability constants, ${}^T\log\,K_{av}$, are consistently lower than the ${}^Tp K_a$ values of PMBP. Separation factors, ${}^T\log\,(K_1/K_2)$ and ${}^T\log\,(K_2/K_3)$, are always found to be positive. The former is well within the expected range which implies little or no steric hindrance to the addition of a second chelate group whereas higher values of ${}^T\log\,(K_2/K_3)$ evidently suggest the presence of an unusual opposition to the formation of a 1 : 3 chelate. In the case of chelating agents having bulky substituents near the donor atoms, such steric hindrance causes K_1/K_2 or K_2/K_3 to be abnormally high. This has been demonstrated for *N*-substituted ethylenediamine complexes of Ni^{2+} [39].

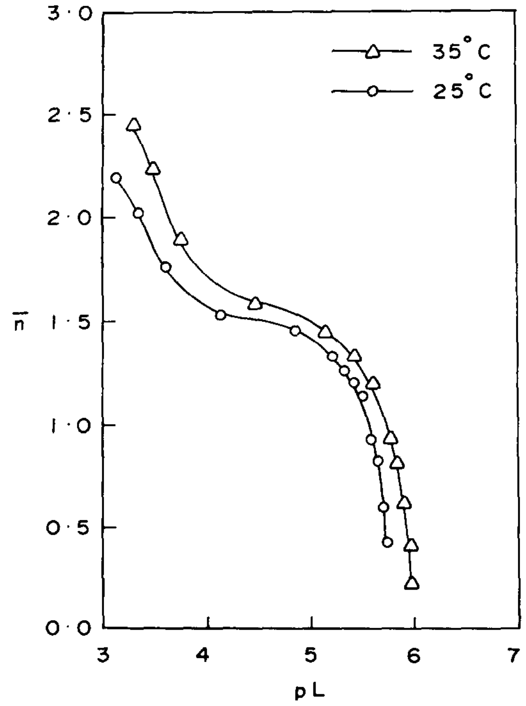

Fig. 1. Formation curves of lanthanum(III) complexes of PMBP.

The formation constants thus evaluated for La^{3+}–PMBP complexes in aqueous dioxane medium permit us to approximate the stability of the lanthanum(III) chelate in water under the same conditions, following the relationship

$$\log \beta_1 - \log \beta_1 \, (\mathrm{W}) = \mathrm{p}K_a - \mathrm{p}K_a(\mathrm{W})$$

proposed by Irving and Rossotti [40] for ML type complexes. Here the

TABLE 1

Thermodynamic stepwise formation constants of La^{3+}–PMBP complexes [a]

Constant	Method of computation [b]	In 70% (v/v) aqueous dioxane		In water	
		25°C	35°C	25°C	35°C
$^{T}\mathrm{pK_a}$	L	6.78	7.09	3.46	3.65
$^{T}\log \beta_1$	L	6.84	7.18	3.52	3.74
	B	6.83	7.10		
	P	7.03	7.23		
$^{T}\log \beta_2$	L	12.10	12.74	5.46	5.86
	B	11.97	12.66		
	P	12.19	12.65		
$^{T}\log \beta_3$	L	14.82	15.03		
	B	NC	NC		
	P	14.53	15.85		
$(^{T}\log K_{av})$ [c]	L	4.94	5.01		
$^{T}\log(K_1/K_2)$ [c]	L	1.58	1.62		
$^{T}\log(K_2/K_3)$ [c]	L	2.54	3.27		

[a] [La^{3+}] = 0.00065 M; [PMBP] = 0.01 M; [N(CH$_3$)$_4$OH] = 0.1 M.

[b] L, values obtained by the least-squares method; maximum scatter in log K_1 or log K_2 is ±0.05, while it is ±0.08 for log K_3; B, values calculated from Bjerrum's half integral method; P, values calculated by point-wise computation. The values of $^{T}\log \beta_n$ are the average of at least 10 titration points.

[c] Values of $^{T}\log K_{av}$, $^{T}\log(K_1/K_2)$ and $^{T}\log(K_2/K_3)$ have been computed from formation constants obtained by least-squares analysis.

NC, not calculable since $\bar{n} < 2.5$.

TABLE 2

Thermodynamic functions of La^{3+}–PMBP complexes in 70% (v/v) aqueous dioxane

Formation constant [a]	ΔG^0 (kcal mol^{-1})		ΔH^0 (kcal mol^{-1})	ΔS^0 (cal K^{-1} mol^{-1})	
	25°C	35°C		25°C	35°C
$^{T}\log \beta_1$	−9.33	−10.13	14.30	79.24	79.27
$^{T}\log \beta_2$	−16.51	−17.97	26.92	145.64	145.65
$^{T}\log \beta_3$	−20.22	−21.20	8.83	97.42	97.44

[a] Thermodynamic functions computed from formation constants obtained by least-squares analysis. The error in ΔG^0 or ΔH^0 lies in the range 0.2–0.5 kcal mol^{-1} and that for ΔS^0 is 0.5 cal K^{-1} mol^{-1}.

symbol (W) represents the corresponding values of β_1 and K_a in water.

Although the above relationship is valid for 1 : 1 complexes, approximations for 1/2 log β_2(W) were also tried using the experimentally obtained log β_2 values. Values of log β_1(W) and log β_2(W) thus calculated are also given in Table 1. The validity of the above relationship has been tested in a recent publication [41] wherein it has been observed that a good approximation on the basis of the above equation could be achieved only for β_1 but which was not so accurate for β_2. Therefore, the extrapolated β_2(W) values given in Table 1 are somewhat uncertain while β_3(W) values have not been computed at all.

Thermodynamic functions

Thermodynamic functions, viz. ΔG^0, ΔH^0 and ΔS^0, associated with La^{3+}–PMBP complexation reactions are summarised in Table 2. The lanthanum(III) chelate of PMBP is formed spontaneously as evidenced by the negative values of the free energies of formation (ΔG^0). The positive values of ligational enthalpy changes (ΔH^0) ensure that the reaction is endothermic. The relatively small ΔH^0 values compared with large values of ΔS^0 indicate entropy as the principal driving force for the formation of metal complexes in aqueous dioxane media. An increase in randomness in the system will increase the stability of complex because entropy is a solvent property. As suggested by Poi and Nancollas [42], ΔG^0 values for 1 : 1 chelates are more negative than the corresponding 1 : 2 or 1 : 3 chelates indicating that mono complexes are energetically more favoured over bis or tris complexes.

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