Thermochimica Acta, 55 (1982) 307–314
Elsevier Scientific Publishing Company, Amsterdam—Printed in The Netherlands

THERMODYNAMICS OF THE COMPLEXING OF URANYL IONS WITH 1-PHENYL-3-METHYL-4-BENZOYLPYRAZOLONE-5 IN AQUEOUS DIOXANE

J.P. SHUKLA, A.K. SABNIS and M.S. SUBRAMANIAN

Radiochemistry Division, Bhabha Atomic Research Centre, Trombay, Bombay-400085 (India)

(Received 25 November 1981)

ABSTRACT

The thermodynamics of the complexing between hexavalent U and 1-phenyl-3-methyl-4-benzoylpyrazolone-5 (PMBP) have been studied in 70 vol% aqueous–dioxane medium at 25 and 35±0.1°C following the Bjerrum–Calvin pH titration technique, as applied by Van Uitert and Haas. The ligand is mono-protonic. The refinement of results of formation constants has been accomplished by the method of least squares treatment 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 stability invariably increases with an increase in temperature both in aqueous as well as aqueous dioxane media. The changes in ΔG^0, ΔH^0 and ΔS^0 at 25 and 35°C for the overall equilibrium constants have also been evaluated. Uranyl complexes of PMBP are entropy stabilized, the values of enthaply changes being positive. Other factors which affect chelate stability are briefly discussed.

INTRODUCTION

Pyrazolones have elicited much interest in recent years owing to their varied medicinal [1,2], analytical [3–7] and commercial applications [8]. Among these, 1-phenyl-3-methyl-4-benzoylpyrazolone-5 (PMBP) displays certain special features which make it one of the most potential extractants for the isolation and separation of several elements [9–19]. The versatility of this reagent is comparable to the more popular extracting agent, 2-thenoyltrifluroacetone (TTA), but excels TTA in terms of its relatively much lower cost [20] and ability to extract most of the metal ions from media of lower pH [6,10,16]. This has prompted several workers to investigate its coordination with a host of metal ions [21–24]. However, not much is known concerning uranium(VI) complexes of PMBP, e.g. composition, structure and stability etc., knowledge of which will be useful using this as an extractant for uranyl ion. To date, no data relative to thermodynamic formation constants of uranyl complexes with PMBP seem to have been reported [25].

As a part of our comprehensive studies on the complexation of uranyl ions with various β diketones [26], the UO_2^{2+} –PMBP system has now been studied in 70% aqueous dioxane at 25 and 35 ± 0.1°C using the Bjerrum–Calvin pH titration technique [27] as applied by Van Uitert and Haas [28]. The lower water solubilities of the reagent as well as its metal derivatives necessitated the use of mixed solvent media. The overall changes in ΔG^0, ΔH^0 and ΔS^0 associated with the complexation reaction have also been evaluated by the temperature coefficient method. Some of the factors affecting M–L stability constants are briefly discussed.

EXPERIMENTAL

All the chemicals used were of A.R. (B.D.H) or G.R. (Merck) grade. Dioxane was purified by the recommended procedure [29]. PMBP was synthesized according to Jensen's method [30] and recrystallised from chloroform to obtain yellow crystals of the enol form (m.p. 92°C, obtained; $C = 73.10$, $H = 5.18$; required for $C_{17}H_{14}N_2O_2$: $C = 73.35$, $H = 5.03$). Uranyl perchlorate was prepared by the reaction of $HClO_4$ with orange uranium trioxide. After crystallization from aqueous acidic solution, the salt was dissolved in 0.01 M $HClO_4$ and the UO_2^{2+} content was determined volumetrically using a Jones Reductor and cerimetric titration. An aqueous solution (10%) of tetramethyl ammonium hydroxide titrant was standardized 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 701 A, which can be read to 0.001 unit of pH.

Titration procedure

A weighed quantity of PMBP, corresponding to a 0.01 M solution in a final volume of 50 ml, was placed in 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 yield a 70 vol.% final composition of dioxane–water in the mixture. Due allowance for the contraction in volume on mixing two solvents was made [31,32].

The titration vessel with its contents was then thermostated at 25 or 35 ± 0.1°C. The glass and calomel electrodes were placed in the titre and titrated by adding small aliquots and noting the pH meter reading. Titrations were repeated until two sets of values differing by only ± 0.01 pH unit were attained. For determining the thermodynamic acid dissociation constants of PMBP, T_pK_a, the same procedure was essentially followed without the addition of metal ion solution [33].

CALCULATIONS

Values of successive formation constants, K_1, K_2 and K_3, for the UO_2^{2+} – PMBP system were evaluated by least squares treatment (rejecting the most divergent data especially for the low values of the $\bar{n}$ function) as given by Albert and Serjeant [34]. Procedural details of the calculations are the same as published elsewhere [26]. The aid of other computational methods, viz. interpolation at half $\bar{n}$ values (Bjerrum's half integral method) as well as point-wise calculation [35] using the following equations, were also utilized for their determinations.

$$\log K_1 = \mathrm{pL} - \log\frac{1-\bar{n}}{\bar{n}}$$

$$\log K_2 = \mathrm{pL} - \log\frac{2-\bar{n}}{\bar{n}-1}$$

$$\log K_3 = \mathrm{pL} - \log\frac{3-\bar{n}}{\bar{n}-2}$$

The mean activity coefficient ($Y\pm$) for the 1:1 electrolyte computed from Harned and Owen's [36] data in 70% dioxane–water medium at different ionic strengths and the 'pH correction factor' [37], log U_H^0, for this medium, needed in the evaluation of thermodynamic constants, are summarized in Table 1. ΔG^0, ΔH^0 and ΔS^0 were calculated as follows

$$\Delta G^0 = -2.303\ RT\ {}^T\log\beta_n$$

$$\Delta H^0 = 42.06\ \left({}^T\log\beta_n^{308.2} - {}^T\log\beta_n^{298.2}\right)$$

TABLE 1

Data on log ($1/Y\pm$) and log U_H^0
medium: 70% (v/v) dioxane–water; log U_H^0 [a]: at 25°C, 0.78, at 35°C, 0.83.

Ionic strength, μ (M)	log ($1/Y\pm$) [b]	
	25°C	35°C
0.001	0.155	0.161
0.002	0.209	0.217
0.003	0.246	0.254
0.004	0.274	0.284
0.005	0.297	0.307
0.006	0.316	0.328
0.007	0.335	0.347
0.008	0.352	0.367
0.009	0.364	0.382

[a] = Ref. 37; [b] = ref. 36.

$\Delta S^0 = \Delta H^0 - \Delta G^0/T$

where all the terms have their usual meaning.

RESULTS AND DISCUSSION

Figure 1 represents the metal — ligand formation curves obtained by plotting pL vs $\bar{n}$ data and do not show flattening at the integral values of $\bar{n}$. These curves extend over the range $0.2 < \bar{n} < 2.6$ indicating the formation of the species UO_2L^+, UO_2L_2 and $UO_2L_3^-$. Values of thermodynamic overall 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 2). It may be mentioned that our values of $^T\log \beta_2$, viz. 12.29 (25°C) agree reasonably well with the "concentration stability constant", $\log \beta_2 = 12.85$ ($\mu = 0.1$, 25°C) reported by Bacher and Keller [22] after making due allowance for different experimental parameters. Compared to graphical methods, these computational methods provide greater statistical accuracy and yield true thermodynamic constants at all points. Results of the determination of T_pK_a of PMBP have been communicated earlier [33]. 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 in triplicate determinations. Variation in the initial concentration of UO_2^{2+} and PMBP gave results with a variation of ± 0.10 log units. An error in measurement of 0.01 pH unit was found to affect the $^T\log \beta_n$ values by approximately 0.1 log unit. There was no evidence of metal ion hydrolysis, polynuclear complexes or protonated complexes.

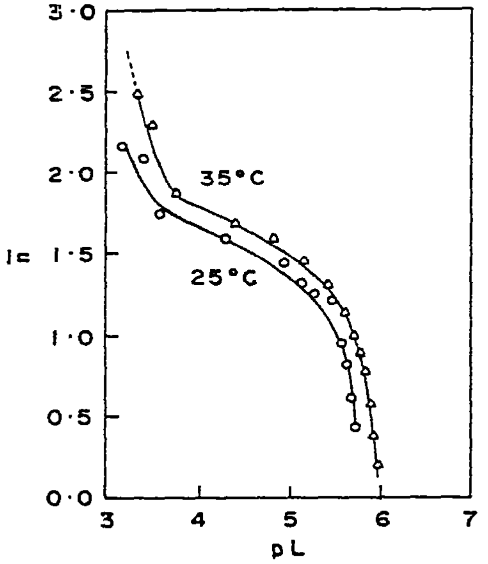

Fig. 1. Formation curves of uranyl complexes of PMBP.

TABLE 2

Thermodynamic step-wise formation constants of UO_2^{2+}–PMBP complexes[a]

Constant	Method of computation[c]	In 70% aqueous dioxane		In water	
		25°C	35°C	25°C	35°C
$^T\mathrm{p}K_a$	L	6.78	7.09	3.46	3.65
$^T\log\beta_1$	L	6.99	7.23	3.67	3.79
	B	6.85	7.10		
	P	7.12	7.26		
$^T\log\beta_2$	L	12.29	12.79	5.65	5.91
	B	12.16	12.68		
	P	12.35	12.60		
$^T\log\beta_3$	L	15.00	15.04		
	B	NC	15.98		
	P	14.75	15.77		
$(^T\log\beta_{\mathrm{ave.}})$[b]	L	5.00	5.01		
$^T\log(K_1/K_2)$[b]	L	1.69	1.67		
$^T\log(K_2/K_3)$[b]	L	2.59	3.31		

[a] $[UO_2^{2+}]=0.001$ M; [PMBP]=0.01 M; $[N(CH_3)_4OH]=0.1$ M.

[b] Values of $^T\log\beta_{\mathrm{ave.}}$, $^T\log(K_1/K_2)$ and $^T\log(K_2/K_3)$ have been computed from formation constants obtained by least squares analysis.

[c] L, Values obtained by 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 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.

NC = Not calculable since $\bar{n}<2.5$.

As normally observed, the average stability constants, $^T\log\ \beta_{\mathrm{ave.}}$ are invariably lower than $T_{\mathrm{p}}K_{\mathrm{a}}$ of PMBP. The ratios of consecutive formation constants $^T\log(K_1/K_2)$ 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 high values of $^T\log(K_2/K_3)$ demonstrate the presence of an unusual opposition to the formation of a 1:3 chelate. While studying uranyl complexes of several substituted β-diketones [26], the formation of 1:3 complexes (anionic) was also observed only with fluorinated β-diketones having relatively lower pK_a whereas unfluorinated β-diketones with higher pK_a formed only 1:2 complexes. This can be easily understood from the fact that the former with lower pK_a will not be able to form covalent bonds as strongly as the latter with their higher basicity. 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 shown for *N*-substituted ethylenediamine complexes of Ni^{2+} [38]. Furthermore, as the tendency of a metal ion to take up a ligand is proportional to the number of vacant sites, the ratio between successive constants is, to a certain extent, statistically determined [39].

The formation constants obtained for UO_2^{2+} –PMBP complexes in aqueous dioxane medium allow us to approximate the stability of the uranyl chelate in water under the same conditions, on the basis of the relation

$$\log\beta_1 - \log\beta_1(w) = pK_a - pK_a(w)$$

given by Irving and Rossotti [40] for ML type complexes. Here the symbol (w) indicates the corresponding values of β_1 and K_a in water.

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

Thermodynamic functions

From Table 3 it is evident that chelation of UO_2^{2+} with PMBP is endothermic which shows that higher temperatures are favourable for complexation. The UO_2^{2+} –PMBP chelate is formed spontaneously as proved by the negative values of ΔG^0. Furthermore, the results in Table 3 show that the entropy change (ΔS^0) accompanying the formation of complexes is positive

TABLE 3

Thermodynamic functions of UO_2^{2+} –PMBP complexes in 70% (v/v) dioxane–water mixture

Formation constant [a]	ΔG^0 (kcal mole^{-1})		ΔH^0 (kcal mole^{-1})	ΔS^0, (cal deg^{-1} mole^{-1})	
	25°C	35°C		25°C	35°C
$^T\log\beta_1$	−9.54	−10.20	10.09	65.83	65.83
$^T\log\beta_2$	−16.77	−18.04	21.03	126.76	126.77
$^T\log\beta_3$	−20.47	−21.21	1.68	74.28	74.27

[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 mole^{-1} and that for ΔS^0 is 0.5 cal deg^{-1} mole^{-1}.

and hence is the driving force for complexation. The very large entropy change is also indicative of the greater availability of coordination sites on uranyl ions. The chemical species in aqueous or partially aqueous solutions, as employed here, are surrounded by a cloud of water molecules with a geometry different from that of bulk water. The complex has a greater hydrated radius and reduced charge and therefore water molecules which are weakly held will be released on complexation by a ligand. Williams [42] opined that where a high entropy of reaction was encountered, a combination of cations and anions was involved. Since the water molecules bound to the metal ion are highly distorted and oriented, their entropy is very low. Thus any process which releases water molecules from this type of strain results in a favourable increase in entropy [43]. The entropy changes accompanying the formation of uranyl complexes are positive for first, second and third steps, demonstrating that the water of hydration is removed during the formation of 1:1, 1:2 as well as 1:3 complexes.

ACKNOWLEDGEMENT

The authors wish to thank the Head of the Radiochemistry Division for his keen interest in this work.

REFERENCES

1 H.G. Garg and C. Prakash, J. Med. Chem., 14 (1971) 175.
2 N.B. Das and A.S. Mitra, Indian J. Chem., 16 B (1978) 638.
3 O. Navratil, Chem. Listy, 68 (1974) 470.
4 Z. Holzbecher, L. Divis, M. Kral, L. Sucha and P. Vlacil, Handbook of Organic Reagents in Inorganic Analysis, Ellis Horwood, Chichestor, 1976, pp. 454, 613, 667.
5 I.R. Efimov, A.K. Nurtaeva and V.M. Peshkova, Zh. Anal. Khim., 32 (1977) 1735.
6 A. Roy and K. Nag, J. Inorg. Nucl. Chem., 40 (1978) 331.
7 S.M. Hasany and I. Hanif, J. Radioanal. Chem., 45 (1978) 115; 47 (1978) 47.
8 R.H. Wiley and P. Wiley, Pyrazolones, Pyrazolidones and Derivatives, John Wiley, New York, 1964.
9 B.F. Myasoedov, N.E. Kochetkova and M.K. Chmutova, Zh. Anal. Khim., 27 (1972) 678; 28 (1973) 1723.
10 G.N. Rao and J.S. Thakur, J. Sci. Ind. Res., 34 (1975) 110.
11 J. Hala and J. Prinoda, Collect. Czech. Chem. Commun., 40 (1975) 546.
12 O. Navratil and A. Malach, Collect. Czech. Chem. Commun., 43 (1978) 2890.
13 M.Y. Mirza and R.T. Bailey, J. Inorg. Nucl. Chem., 41 (1979) 772.
14 O. Navratil, Collect. Czech. Chem. Commun., 45 (1980) 1221.
15 M.Y. Mirza and F.I. Nwabue, Radiochim. Acta, 27 (1980) 47.
16 S. Umetani, M. Matsui, J. Toei and T. Shigematsu, Anal. Chim. Acta, 113 (1980) 315.
17 M.S. Bhatti and I.H. Qureshi, J. Radioanal. Chem., 56 (1980) 65.
18 M.Y. Mirza and F.I. Nwabue, Talanta, 28 (1981) 49.
19 Y. Akama, T. Nakai and F. Kawamura, Analyst, 106 (1981) 250.

20 Yu. A. Zolotov. Extraction of Chelate Compounds Ann Arbor-Humphrey Scientific Publishers, 1970, p. 227 (Engl. translation).
21 B.S. Jensen, Acta Chem. Scand., 13 (1959) 1890.
22 W. Bacher and C. Keller. J. Inorg. Nucl Chem., 35 (1973) 2945.
23 A. Roy and K. Nag, Bull. Chem. Soc. Jpn., 51 (1978) 1525.
24 O. Navratil and P. Linhart, Collect. Czech. Chem. Commun., 45 (1980) 1221.
25 L.G. Sillen and A.E. Martell, Stability Constants of Metal-Ion Complexes, Sect. II, Suppl. 1, The Chemical Society, London, 1964, 1971.
26 J.P. Shukla, V.K. Manchanda and M.S. Subramanian, J. Electroanal. Chem., 50 (1974) 253.
27 M. Calvin and N.C. Melchior, J. Am. Chem. Soc., 70 (1948) 3270.
28 L.G. Van Uitert and C.G. Haas, J. Am. Chem. Soc., 75 (1953) 451.
29 A. Weissberger and E.S. Proskauer, Organic Solvents, Vol. 7, Intersceince, New York, 1955, p. 139.
30 B.S. Jensen, Acta Chem. Scand., 13 (1959) 1668.
31 H. Irving and H.S. Rossotti, J. Chem. Soc., (1954) 2910.
32 H. Irving and U.S. Mahnot, J. Inorg. Nucl. Chem., 30 (1968) 1215.
33 J.P. Shukla, A.K. Sabnis and M.S. Subramanian, Thermochim. Acta, 49 (1981) 361.
34 A. Albert and E.P. Serjeant, Ionization Constants of Acids and Bases, Methuen, London, 1962, p. 165.
35 H. Irving and H.S. Rossotti, J. Chem. Soc., (1953) 3397; (1954) 2904.
36 H.S. Harned and B.B. Owen, The Physical Chemistry of Electrolytic Solutions, Reinhold, New York, 1958, pp. 713–718.
37 J.P. Shukla and S.G. Tandon, J. Electroanal. Chem., 35 (1972) 423.
38 F. Basolo and R.K. Murman, J. Am. Chem. Soc., 74 (1952) 5243; 76 (1954) 211.
39 J. Bjerrum, Metal Amine Formation in Aqueous Solutions, P. Haase, Copenhagen, 1941.
40 H. Irving and H.S. Rossotti, Acta Chem. Scand., 10 (1956) 72.
41 J. Horak, Z. Finta and Cs. Varhelyi, J. Inorg. Nucl. Chem., 43 (1981) 111.
42 R.J.P. Williams, J. Phys. Chem., 58 (1954) 121.
43 I. Grenthe, Acta Chem. Scand., 18 (1964) 293.