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Chelation Behaviour of Ce(III), Th(IV), and UO_2(VI) with 5,7-Dihydroxy-6-formyl-2-methylbenzopyran-4-one *Schiff* Bases

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Summary. The stability constants of the stepwise chelate formation between Ce^{3+}, Th^{4+}, and UO_2^{2+} ions and some *Schiff* bases derived from 5,7-dihydroxy-6-formyl-2-methylbenzopyran-4-one were determined conductometrically as well as potentiometrically applying the *Irving* and *Rossotti* techniques. The results indicate the formation of 1:1 and 1:2 (*M*:*L*) chelates. The stability constants increase with decreasing ionic strength, decreasing temperature, and decreasing percentage of ethanol. In different organic solvents (70% v/v solvent-water media), the stability constant values follow the order MeOH < EtOH < 1-propanol < 2-propanol < acetone < *DMSO* depending on both the dielectric constant and the hydrogen bonding structure of the medium. The thermodynamic parameters (ΔG, ΔH, and ΔS) were calculated; they indicate that the chelate formation is an exothermic process and that the degree of disorder of the solution increases upon chelation.

Keywords. Ce^{3+}; Th^{4+}; UO_2^{2+}; *Schiff* bases; Chromone.

Das Chelierungsverhalten von Ce^{3+}, Th^{4+} und UO_2^{2+} mit *Schiff*schen Basen vom Typ 5,7-Dihydroxy-6-formyl-2-methylbenzopyran-4-on

Zusammenfassung. Die Stabilitätskonstanten für die stufenweise Chelatbildung von Ce^{3+}-, Th^{4+}- und UO_2^{2+}-Ionen mit von 5,7-Dihydroxy-6-formyl-2-methylbenzopyran-4-onen abgeleiteten *Schiff*schen Basen wurden konduktometrisch und potentiometrisch mit Hilfe der *Irving*-*Rossotti*-Technik bestimmt. Die Ergebnisse zeigen die Bildung von 1:1- und 1:2-Chelaten (*M*:*L*) an. Die Stabilitäkonstanten steigen mit steigender Ionenstärke, abnehmender Temperatur und abnehmendem Anteil von Ethanol. In verschiedenen organischen Lösungsmitteln (70% v/v Lösungsmittel-Wasser-Gemische) folgen die Stabilitätskonstanten der Reihe MeOH < EtOH < 1-Propanol < 2-Propanol < Aceton < *DMSO*, hängen also sowohl von der Dielektrizitätskonstante als auch von der Wasserstoffbrückenbindungsstruktur des Mediums ab. Die thermodynamischen Parameter (ΔG, ΔH und ΔS) wurden bestimmt; sie weisen darauf hin, daß die Bildung solcher Chelate exotherm verläuft und daß und der Unordnungsgrad der Lösung bei der Chelierung steigt.

Introduction

The condensation of primary amines with carbonyl compounds yields *Schiff* bases [1, 2]. The complexation of *Schiff* bases with lanthanides has been the subject of

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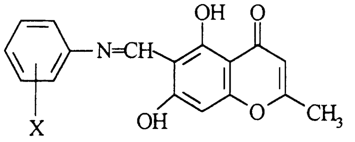

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X = H (**a**), *o*-COOH (**b**), *o*-OH (**c**), *o*-OH, *m*-Cl (**d**), *o*-OH, *p*-SO_3H (**e**)

Scheme 1

many investigations [3–11] including determination of stepwise and overall formation constants and evaluation of the effects of ionic strength and temperature of the medium on the stability of the chelates.

The present paper deals with conductometric and potentiometric studies of the chelates of Ce^{3+}, Th^{4+}, and UO_2^{2+} with *Schiff* bases prepared from 5,7-dihydroxy-6-formyl-2-methylbenzopyran-4-one and aniline, anthranilic acid, *o*-aminophenol, 2-amino-5-chlorophenol, and 4-amino-3-hydroxybenzenesulfonic acid (Scheme 1). The conductometric titrations were carried out in 70% (v/v) ethanol-water whereas the potentiometric titrations were performed according to *Irving* and *Rossotti* [12] at different ionic strengths (0.14, 0.10, 0.06, and 0.02 *M* NaCl) and different temperatures (55, 45, 35, and 25°C). The effects of varying alcohol content (90, 80, 70, and 60% (v/v)) and different solvents (methanol, ethanol, 1-propanol, 2-propanol, acetone, and *DMSO*) on the stability constants of the metal chelates were also studied. The thermodynamic parameters (ΔG, ΔH, and ΔS) of the formed chelates were calculated.

Results and Discussion

Conductometric titration curves indicate that the increase of conductance upon addition of metal ion solution is mainly due to the release of H^+ ions. Taking the chelation behaviour of Ce^{3+} with **1a** as an example, one can formulate

$$2H_2L + Ce^{3+} \rightleftharpoons 2H^+ + [Ce(HL)_2]^+$$

Further addition of metal ions beyond complete conversion of H*L* to an 1:2 species will produce a new 1:1 species according to

$$[Ce(HL)_2]^+ + Ce^{3+} \rightleftharpoons 2[CeL]^+ + 2H^+$$

The *Schiff* bases possess two centers of chelation. The first one stems from the azomethine group and the OH group in its *ortho* position, and the second one involves the chromone carbonyl group in position 4 and the deprotonated hydroxy group in position 5. Accordingly, addition of metal ions to the 1:1 *ML* species results in a new 2:1 M_2L species:

$$[CeL]^+ + Ce^{3+} \rightleftharpoons [Ce_2L]^{4+}$$

The conductometric titration curves for the complexes show three breaks (Fig. 1) at molar ratios of 2:1, 1:1, and 1:2, indicating the formation of three types of complexes with stoichiometric ratios 2:1, 1:1, and 1:2 (*M*:*L*). Higher molar

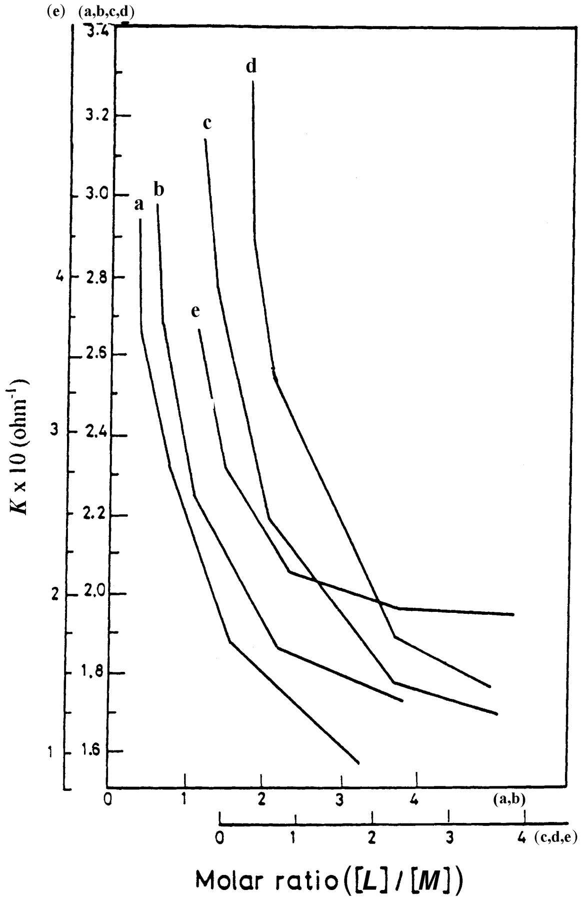

Fig. 1. Conductometric titration curves for $4 \times 10^{-5}M$ solutions of *Schiff* bases **1a–e** with $10^{-3}M$ Th^{4+} ions

ratios can be excluded due to steric hindrance generated upon accommodating more than two *Schiff* base molecules around the metal ion. The stability constants of the 1:1 and 1:2 chelates ($\log\beta_1$ and $\log\beta_2$) were calculated from *pH*-metric titration results.

From the *pH* titration curves of the mixtures containing *Schiff* bases and metal ions, the average number of ligand molecules attached to a metal ion ($\bar{n}$) and the free ligand exponent (*pL*) were calculated and plotted against each other, thus affording the formation curves of the metal complexes (Fig. 2). The $\bar{n}$ values never exceed 2 for all complexes, indicating the formation of 1:1 and 1:2 (*M*:*L*) complexes only. The possibility of formation of binuclear chelates was considered negligible due to the very low concentrations of the metal ions used (10^{-4} *M*) [13]. The stability constants of the complexes were studied with respect to the effect of ionic strength, temperature, ethanol percentage, and solvent type. Under all conditions, the stability constant values exhibit the following decreasing order [14]: $Th^{4+} > Ce^{3+} > UO_2^{2+}$. This can be attributed to the decrease of charge on the central metal ion [15] which decreases the electrostatic attraction between the cation and the *Schiff* base.

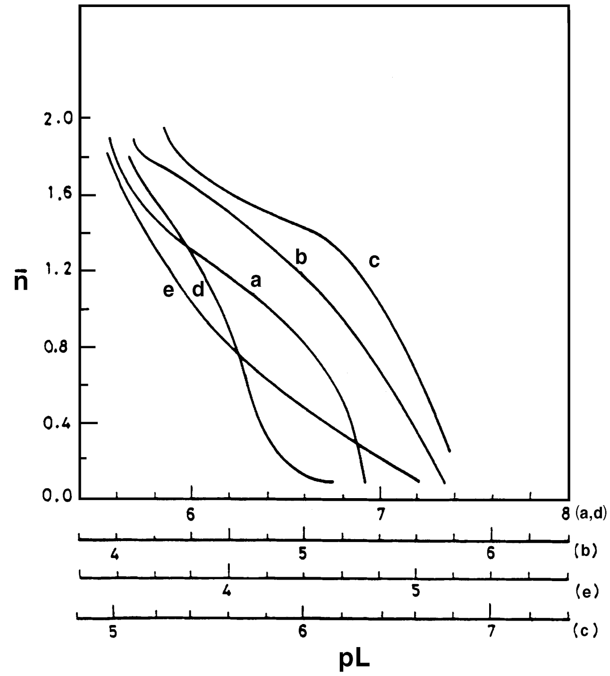

Fig. 2. Formation curves of UO_2^{2+} chelates with *Schiff* bases **1a–e** (0.106 *M* NaCl, 298 K) in 70% v/v ethanol-water

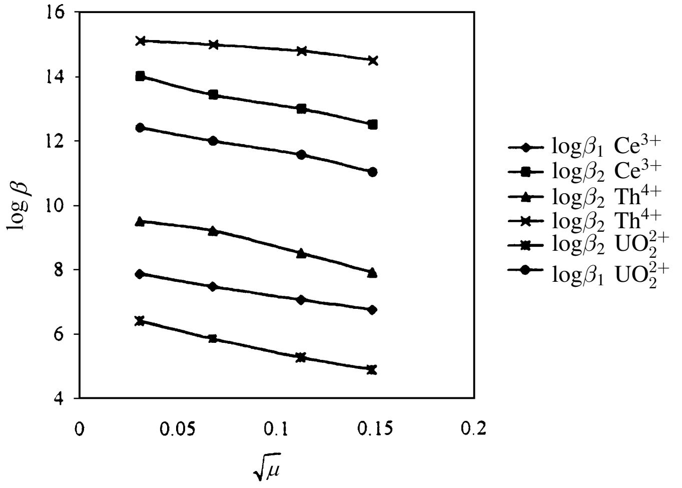

Fig. 3. Plots of logβ_1 and logβ_2 (mean values) *vs* $\sqrt{\mu}$ for chelates of **1a** with Ce^{3+}, Th^{4+}, and UO_2^{2+} at 298 K (70% v/v ethanol-water)

In case of Ce^{3+} and Th^{4+} chelates, the stability constants follow the order **1c** >**1d** >**1a** >**1b** >**1e**, whereas in the case of UO_2^{2+} chelates the order is **1c** > **1a** > **1d** >**1b** >**1e**. This behaviour correlates with the effect of substitution on the phenyl ring as follows:

1) The high stability of *Schiff* base **1c** complexes can be attributed to the presence of the OH group in the o'-position relative to the azomethine group, forming a

Table 1. logβ_1 and logβ_2 values for Ce^{3+}, Th^{4+}, and UO$_2^{2+}$ chelates with *Schiff* bases **1a–e** at different ionic strengths

	μ (NaCl)	Ce^{3+}				Th^{4+}				UO$_2^{2+}$			
		logβ_1		logβ_2		logβ_1		logβ_2		logβ_1		logβ_2	
		mean value	SD	mean value	SD	mean value	SD	mean value	SD	mean value	SD	mean value	SD
1a	0.146	6.73	0.02	12.08	0.02	6.84	0.03	13.58	0.03	6.30	0.03	11.02	0.01
1b		5.37	0.03	9.98	0.02	5.52	0.02	11.01	0.02	5.13	0.02	9.82	0.02
1c		7.02	0.03	13.21	0.04	7.63	0.03	14.84	0.03	6.57	0.03	11.98	0.03
1d		6.79	0.01	12.84	0.03	7.54	0.04	14.69	0.02	6.12	0.03	11.12	0.02
1e		4.42	0.03	8.38	0.02	5.35	0.03	10.03	0.02	4.05	0.01	7.80	0.02
1a	0.106	7.04	0.03	12.64	0.01	7.30	0.02	14.06	0.02	6.68	0.02	12.55	0.03
1b		5.63	0.03	10.45	0.03	5.85	0.01	11.42	0.02	5.54	0.05	10.17	0.03
1c		7.34	0.05	13.85	0.01	7.98	0.02	15.74	0.02	6.76	0.02	12.66	0.02
1d		7.10	0.04	13.23	0.03	7.88	0.02	15.50	0.03	6.33	0.04	12.07	0.03
1e		4.71	0.02	8.86	0.04	5.64	0.03	10.44	0.02	4.37	0.04	7.84	0.02
1a	0.066	7.47	0.03	12.99	0.02	7.81	0.02	14.39	0.02	7.00	0.03	12.90	0.02
1b		6.00	0.02	11.25	0.02	6.22	0.03	11.81	0.03	5.81	0.02	10.98	0.03
1c		7.66	0.01	14.66	0.03	8.51	0.02	16.71	0.50	7.01	0.02	12.92	0.02
1d		7.29	0.04	13.94	4.99	8.37	0.03	15.52	0.51	6.79	0.03	12.02	0.03
1e		5.02	0.03	9.26	0.03	6.20	0.02	10.72	0.02	4.77	0.02	8.62	0.03
1a	0.026	7.86	0.03	14.68	0.03	8.33	0.02	15.11	0.01	7.23	0.02	13.33	0.02
1b		6.40	0.04	12.08	0.04	6.76	0.02	12.94	0.04	6.17	0.03	11.84	0.02
1c		7.98	0.03	15.23	0.02	8.83	0.03	17.22	0.02	7.40	0.03	14.20	0.02
1d		7.59	0.02	14.29	0.04	8.74	0.03	16.92	0.02	7.11	0.02	13.29	0.03
1e		5.35	0.03	10.15	0.04	6.80	0.02	10.89	0.03	5.22	0.03	10.00	0.03
1a	0.00[a]	8.52	0.02	15.51	0.03	9.29	0.03	17.40	0.02	7.86	0.12	15.17	0.02
1b		7.12	0.04	13.48	0.03	7.51	1.16	14.01	0.02	6.84	0.03	13.07	0.04
1c		8.64	0.02	16.55	0.04	9.68	0.02	18.48	0.02	7.78	0.01	14.91	0.02
1d		8.11	0.03	15.21	0.04	9.50	0.03	18.12	0.03	7.67	0.03	14.63	0.04
1e		5.94	0.04	11.19	0.05	7.69	0.04	11.53	0.02	5.91	0.02	11.16	0.04

SD: standard deviation; mean values obtained by interpolation at half $\bar{n}$, successive approximation, and mid point methods; [a]logβ values obtained by linear regression analysis

new reactive center for chelation through *NO′*; the double chelation through *NOO′* contributes to the complex stability.

2) The lower stability of **1d** chelates is caused by the *-I* effect of the Cl atom *para* to the OH group in the anilino ring which decreases the electron density around the OH group, thus decreasing its ability for chelation and therefore the stability of the complexes. In case of Ce^{3+} and Th^{4+}, the small size of these ions renders them unaffected by the steric effect of the Cl atom, and their complexes with **1d**

Table 2. logβ_1 and logβ_2 values for Ce^{3+}, Th^{4+}, and UO_2^{2+} chelates with *Schiff* bases **1a–e** at different temperatures

	T (K)	Ce^{3+}				Th^{4+}				UO_2^{2+}			
		logβ_1		logβ_2		logβ_1		logβ_2		logβ_1		logβ_2	
		mean value	SD	mean value	SD	mean value	SD	mean value	SD	mean value	SD	mean value	SD
1a	328	6.11	0.01	11.10	0.04	6.44	0.02	12.70	0.02	5.99	0.02	11.11	0.01
1b		4.91	0.04	9.23	0.02	5.12	0.02	9.88	0.02	5.00	0.01	8.77	0.04
1c		6.37	0.06	11.96	0.01	7.18	0.01	13.71	0.01	6.04	0.06	11.33	0.01
1d		6.24	0.03	11.83	0.02	6.95	1.01	13.54	1.01	5.55	0.02	10.75	0.02
1e		4.11	0.05	7.95	0.03	4.92	0.02	9.38	0.02	3.92	0.02	6.67	0.03
1a	318	6.31	0.03	11.48	0.02	6.74	0.02	13.15	0.02	6.19	0.02	11.55	0.02
1b		5.12	0.03	9.62	0.01	5.35	0.01	10.29	0.01	5.17	0.03	9.28	0.26
1c		6.63	0.03	12.82	0.03	7.43	0.05	14.25	0.05	6.26	0.03	11.81	0.02
1d		6.43	0.05	12.19	0.02	7.25	0.02	14.10	0.02	5.75	0.02	11.12	0.02
1e		4.27	0.04	8.23	0.05	5.09	0.03	9.70	0.03	4.06	0.04	6.99	0.03
1a	308	6.64	0.03	11.90	0.02	7.02	0.02	13.60	0.02	6.42	0.02	11.95	0.03
1b		5.39	0.02	10.03	0.04	5.60	0.02	10.80	0.02	5.35	0.01	9.78	0.03
1c		7.10	0.02	13.30	0.02	7.71	0.04	14.99	0.04	6.48	0.03	12.22	0.04
1d		6.75	0.05	12.65	0.03	7.50	0.01	14.99	0.01	6.04	0.03	11.50	0.02
1e		4.52	0.04	8.52	0.03	5.27	0.03	10.04	0.03	4.22	0.02	7.23	0.03
1a	298	7.04	0.01	12.54	0.01	7.30	0.02	14.06	0.02	6.68	0.02	12.55	0.02
1b		5.63	0.03	10.45	0.02	5.85	0.01	11.42	0.01	5.54	0.04	10.17	0.03
1c		7.34	0.02	13.85	0.01	7.98	0.02	15.74	0.02	6.76	0.02	12.66	0.03
1d		7.10	0.04	13.23	0.02	7.88	0.02	15.50	0.02	6.33	0.03	12.07	0.03
1e		4.71	0.02	8.86	0.03	5.64	0.02	10.44	0.02	4.37	0.03	7.84	0.07
1a	273[a]	7.86	0.04	13.18	0.03	7.74	0.01	15.74	0.01	7.25	0.01	13.64	0.02
1b		6.21	0.02	11.47	0.02	6.35	0.03	12.59	0.03	5.96	0.01	11.47	0.01
1c		8.22	0.04	15.75	0.03	8.39	0.02	17.48	0.02	7.18	0.03	13.78	0.02
1d		7.83	0.03	14.67	0.01	8.41	0.02	17.09	0.02	6.81	0.02	12.91	0.02
1e		5.22	0.03	9.51	0.03	6.10	0.03	11.20	0.03	4.80	0.03	9.05	0.04

SD: standard deviation; mean values obtained by interpolation at half $\bar{n}$, successive approximation, and mid point methods; [a]logβ values obtained by linear regression analysis

are more stable than those with **1a**. In case of the UO_2^{2+} ion, its large diameter [16] in combination with the bulky Cl atom decreases the stability of UO_2^{2+} -**1d** chelates due to steric effects; hence, the stability of UO_2^{2+} complexes with **1d** is lower than that of its complexes with **1a**.

3) The lower stability of **1b** chelates relative to those of **1c** can be attributed to their lower pK_a values (**1b**: 6.42, 7.30, and 9.44; **1c**: 6.70, 8.26, and 11.22), indicating an increase of the ionic character of the **1b** chelates and therefore point to facilitated hydrolysis.

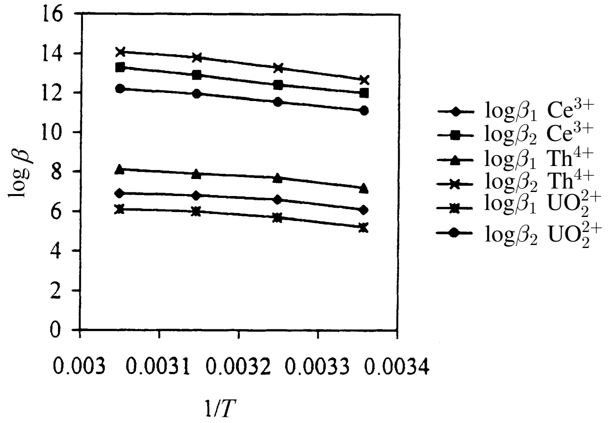

Fig. 4. Plots of logβ_1 and logβ_2 mean values *vs* 1/T for chelates of **1a** with Ce^{3+}, Th^{4+} and UO_2^{2+} 0.106 M NaCl 70% v/v ethanol-water

4) The electron withdrawing effect of the bulky SO_3H group in *p*-position of the azomethine group (in addition to the OH group in *o*-position to the -CH = N- group) decreases the stability of **1e** chelates.

The ionic strength of solutions is related to the activity coefficient [17] according to $\log f = A^2 \cdot Z_i^2 \cdot \mu^{1/2}$ where f is the activity coefficient, A is a constant, and Z_i is the ionic charge. Therefore, an increase in ionic strength will decrease the activity coefficient and, consequently, the activity of the ions. The tendency for chelation thus decreases as reflected by the decreasing stability constants of the metal chelates. This is in full agreement with the *Debye-Hückel* equation ([18]; $\log\beta = \log\beta^\circ - (0.509 Z^2 \sqrt{\mu}/(1 + \alpha\sqrt{\mu}))$; μ: ionic strength of the medium, β: stability constant at a given ionic strength, β°: thermodynamic formation constant at zero ionic strength, α: activity coefficient).

Thermodynamic formation constants (at $\mu = 0$) were obtained by applying linear regression analysis. The plot of logβ_1 and logβ_2 *vs.* $\sqrt{\mu}$ (Fig. 3) is linear with a variation coefficient ≥ 0.98 [16]. The obtained results are listed in Table 1.

The values of logβ_1 and logβ_2 at different temperatures (Table 2) show that the stability constants of the complexes decrease with increasing temperature. This can be attributed to the thermal hydrolysis of the metal complexes [18]. The values of ΔG for the ionization process can be calculated from Eq. (1) [20]:

$$-\Delta G = 2.303 \mathrm{R} T \log\beta \qquad (1)$$

Substituting in $\Delta G = \Delta H - T\Delta S$ and resolving for logβ affords Eq. (2) [19]:

$$\log\beta = \Delta S/2.303R - \Delta H/2.303R \cdot 1/T \qquad (2)$$

A plot of logβ *vs.* $1/T$ therefore gives a straight line (Fig. 4; variation coefficient ≥ 0.97) with a slope of ΔH/2.303R and an intercept of ΔS/2.303R.

The negative values of both ΔG and ΔH indicate that the complexation reaction is exothermic. All ΔS values are positive due to displacement of the

Table 3. Thermodynamic parameters of Ce^{3+} chelates with *Schiff* bases **1a–e**

		mean value	T (K)	$-\Delta G$ ($kJ \cdot mol^{-1}$)	$-\Delta H$ ($kJ \cdot mol^{-1}$)	ΔS ($J \cdot mol^{-1} \cdot K^{-1}$)
1a	$\log\beta_1$	6.11	328	38.31	52.42	114.69
		6.31	318	38.36		
		6.64	308	39.09		
		7.04	298	40.10		
	$\log\beta_2$	11.10	328	69.59	63.78	224.60
		11.48	318	69.78		
		11.90	308	70.06		
		12.54	298	71.43		
1b	$\log\beta_1$	4.91	328	30.78	36.89	91.75
		5.12	318	31.12		
		5.39	308	31.73		
		5.63	298	32.07		
	$\log\beta_2$	9.23	328	57.88	69.17	176.81
		9.62	318	58.48		
		10.03	308	59.05		
		10.45	298	59.53		
1c	$\log\beta_1$	6.37	328	39.94	51.42	124.25
		6.63	318	40.30		
		7.10	308	41.80		
		7.34	298	41.81		
	$\log\beta_2$	11.96	328	74.99	98.10	236.07
		12.82	318	77.93		
		13.30	308	78.30		
		13.85	298	78.89		
1d	$\log\beta_1$	6.24	328	39.12	47.34	120.42
		6.53	318	39.69		
		6.75	308	39.74		
		7.10	298	40.44		
	$\log\beta_2$	11.83	328	74.17	78.12	223.64
		12.19	318	74.11		
		12.65	308	74.48		
		13.23	298	75.36		
1e	$\log\beta_1$	4.11	328	25.77	45.87	79.33
		4.27	318	25.96		
		4.52	308	26.61		
		4.71	298	26.83		
	$\log\beta_2$	7.95	328	49.84	51.90	151.01
		8.23	318	50.03		
		8.52	308	50.16		
		8.86	298	50.47		

Table 4. Thermodynamic parameters of Th^{4+} chelates with *Schiff* bases **1a–e**

		mean value	T (K)	$-\Delta G$ ($kJ \cdot mol^{-1}$)	$-\Delta H$ ($kJ \cdot mol^{-1}$)	ΔS ($J \cdot mol^{-1} \cdot K^{-1}$)
1a	$\log\beta_1$	6.44	328	40.38	41.50	127.11
		6.74	318	40.97		
		7.02	308	41.33		
		7.30	298	41.58		
	$\log\beta_2$	12.70	328	79.63	63.72	242.76
		13.15	318	79.93		
		13.60	308	80.07		
		14.08	298	80.19		
1b	$\log\beta_1$	5.12	328	32.14	57.34	98.44
		5.35	318	32.56		
		5.60	308	32.97		
		5.85	298	33.36		
	$\log\beta_2$	9.88	328	62.02	69.05	192.11
		10.29	318	62.55		
		10.80	308	63.66		
		11.42	298	65.13		
1c	$\log\beta_1$	7.18	328	45.02	44.11	135.72
		7.43	318	45.16		
		7.71	308	45.39		
		7.98	298	45.46		
	$\log\beta_2$	13.71	328	86.06	99.60	256.14
		14.25	318	86.62		
		14.99	308	88.25		
		15.74	298	89.66		
1d	$\log\beta_1$	6.95	328	43.57	51.07	131.89
		7.25	318	44.07		
		7.50	308	44.16		
		7.88	298	44.89		
	$\log\beta_2$	13.54	328	84.89	121.37	262.83
		14.10	318	85.71		
		14.88	308	87.62		
		15.50	298	88.29		
1e	$\log\beta_1$	4.92	328	30.85	39.34	94.62
		5.09	318	30.94		
		5.27	308	31.03		
		5.64	298	32.13		
	$\log\beta_2$	9.38	328	58.81	56.22	176.81
		9.70	318	59.03		
		10.04	308	59.11		
		10.44	298	59.47		

Table 5. Thermodynamic parameters of UO_2^{2+} chelates with *Schiff* bases **1a–e**

		mean value	T (K)	$-\Delta G$ ($kJ \cdot mol^{-1}$)	$-\Delta H$ ($kJ \cdot mol^{-1}$)	ΔS ($J \cdot mol^{-1} \cdot K^{-1}$)
1a	$\log\beta_1$	5.99	328	37.56	31.86	113.73
		6.19	318	37.63		
		6.42	308	37.80		
		6.68	298	38.05		
	$\log\beta_2$	11.14	328	69.84	63.72	212.18
		11.55	318	70.21		
		11.95	308	70.35		
		12.55	298	71.49		
1b	$\log\beta_1$	5.00	328	31.35	22.85	94.62
		5.17	318	31.43		
		5.35	308	31.50		
		5.54	298	31.56		
	$\log\beta_2$	8.77	328	54.99	50.97	214.09
		9.28	318	56.41		
		9.78	308	57.58		
		10.17	298	57.93		
1c	$\log\beta_1$	6.04	328	37.87	29.41	115.65
		6.26	318	38.05		
		6.48	308	38.15		
		6.76	298	38.51		
	$\log\beta_2$	11.33	328	71.04	63.72	215.04
		11.81	318	71.79		
		12.22	308	71.94		
		12.66	298	72.11		
1d	$\log\beta_1$	5.55	328	34.80	33.73	104.18
		5.75	318	34.95		
		6.04	308	35.56		
		6.33	298	36.06		
	$\log\beta_2$	10.75	328	67.40	65.71	194.97
		11.12	318	67.60		
		11.50	308	67.71		
		12.07	298	68.75		
1e	$\log\beta_1$	3.92	328	24.58	20.78	74.55
		4.06	318	24.68		
		4.22	308	24.85		
		4.37	298	24.89		
	$\log\beta_2$	6.67	328	41.82	38.23	205.49
		6.99	318	42.49		
		7.23	308	42.57		
		7.84	298	44.66		

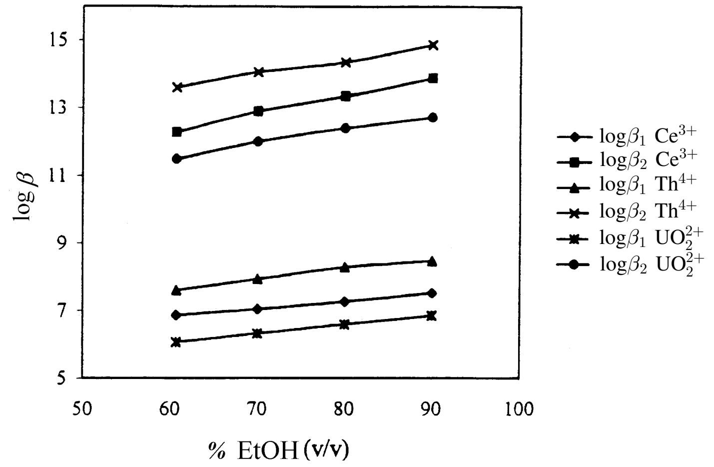

Fig. 5. Plots of logβ_1 and logβ_2 (mean values) *vs.* percentage of ethanol for chelates of **1a–e** with Ce^{3+}, Th^{4+}, and UO_2^{2+} at 0.106 *M* NaCl and 298 K

highly oriented and ordered water molecules by *Schiff* base molecules, thus increasing the disorder in the solution by complexation.

The stability constants at 273 K were obtained applying linear regression analysis. The plots of logβ_1 and logβ_2 *vs.* T give straight lines with correlation coefficients $\geq$0.98. The stability constant temperature coefficient (rate of change of logβ with temperature) ranged between 0.01 and 0.03.

The investigation of solvent effects on the stability constants of the metal chelates was carried out in different ethanol-water compositions and in different solvents. The results, listed in Table 6, show that as the percentage of ethanol increases the stability constants of the complexes also increase. This can be attributed to the higher solvation ability of water as compared to ethanol that may compete with *Schiff* bases in terms of coordination with the metal cation. In addition, the lower dielectric constant of ethanol may also increase the electrostatic contribution of the metal-*Schiff* base bond formation, thus leading to an increase of the stability constants with its increasing amount in solvent mixture [21]. The plot of logβ *vs.* ethanol percentage gives a straight line (Fig. 5) [22]. The stability constants of the chelates in pure ethanol and pure water are obtained by linear regression analysis.

The dielectric constant of any solvent-water medium can be calculated using Eq. (3) where D is the dielectric constant and n is the mole fraction:

$$D(\text{medium}) = (D(\text{solvent}) \times n(\text{solvent})) + (D(\text{water}) \times n(\text{water})) \qquad (3)$$

The stability constants of metal-*Schiff* base chelates in different solvents of varying polarities (dielectric constants: MeOH, 32.62; EtOH, 24.3; 1-propanol, 20.1; 2-propanol, 18.3; acetone, 20.7; *DMSO*, 4.7) increase following the sequence MeOH < EtOH < 1-propanol < 2-propanol < acetone < *DMSO* (Table 7), indicating that the dielectric constant of the medium is not the predominant factor affecting the change of logβ values since their relationship is not linear. This can be attributed to the dependence of the stability constants on both the dielectric

Table 6. logβ_1 and logβ_2 values for Ce^{3+}, Th^{4+}, and UO_2^{2+} chelates with *Schiff* bases **1a–e** at different percentages of ethanol

	%EtOH	Ce^{3+}				Th^{4+}				UO_2^{2+}			
		logβ_1		logβ_2		logβ_1		logβ_2		logβ_1		logβ_2	
		mean value	SD	mean value	SD	mean value	SD	mean value	SD	mean value	SD	mean value	SD
1a	60	6.87	0.02	12.27	0.02	7.17	0.02	13.93	0.03	6.47	0.03	11.79	0.03
1b		5.51	0.02	10.16	0.02	5.66	0.02	10.82	0.03	5.36	0.03	9.79	0.05
1c		7.22	0.02	13.43	0.02	7.78	0.02	15.09	0.02	6.65	0.03	11.99	0.03
1d		6.83	0.01	13.15	0.02	7.63	0.02	14.84	0.03	6.20	0.02	11.54	0.01
1e		4.60	0.02	8.62	0.02	5.51	0.01	10.72	0.02	4.28	0.01	7.43	0.01
1a	70	7.04	0.02	12.54	0.01	7.30	0.02	14.06	0.02	6.68	0.02	12.55	0.03
1b		5.63	0.02	10.45	0.03	5.85	0.01	11.42	0.02	5.54	0.04	10.17	0.03
1c		7.34	0.02	13.85	0.01	7.98	0.02	15.74	0.02	6.76	0.02	12.66	0.02
1d		7.10	0.02	13.23	0.03	7.88	0.02	15.50	0.03	6.33	0.03	12.07	0.03
1e		4.71	0.02	8.86	0.04	5.64	0.02	10.44	0.02	4.37	0.03	7.84	0.01
1a	80	7.26	0.02	12.97	0.01	7.43	0.02	14.35	0.04	6.84	0.03	12.72	0.02
1b		5.80	0.03	11.20	0.03	6.10	0.02	11.94	0.03	5.82	0.01	10.97	0.02
1c		7.62	0.03	14.85	0.04	8.20	0.03	15.94	0.02	7.12	0.02	13.09	0.01
1d		7.46	0.03	14.17	0.02	8.10	0.02	15.75	0.02	6.52	0.02	12.56	0.03
1e		4.99	0.03	9.34	0.02	5.83	0.01	11.41	0.03	4.69	0.02	8.77	0.02
1a	90	7.53	0.03	13.88	0.03	7.69	0.02	14.88	0.03	7.08	0.02	13.49	0.02
1b		6.36	0.02	11.92	0.03	6.45	0.02	12.13	0.03	6.52	0.02	11.47	0.02
1c		7.98	0.01	15.07	0.02	8.57	0.02	16.82	0.03	7.76	0.21	13.60	0.01
1d		7.86	0.02	14.93	0.01	8.37	0.03	16.20	0.02	6.94	0.02	13.01	0.01
1e		5.32	0.02	10.23	0.02	6.00	0.03	11.97	0.02	5.22	0.02	9.50	0.01
1a	100[a]	7.74	0.02	15.75	0.04	6.06	0.03	15.10	0.03	7.46	0.00	14.77	0.03
1b		6.50	0.05	12.44	0.03	6.66	0.03	12.67	0.02	6.74	0.01	12.00	0.02
1c		8.18	0.01	15.78	0.03	8.76	0.02	17.27	0.03	8.00	0.02	14.98	0.02
1d		8.17	0.01	15.41	0.03	8.62	0.01	16.66	0.01	7.07	0.02	13.37	0.02
1e		5.52	0.02	10.58	0.02	6.18	0.02	12.26	0.03	5.54	0.01	10.17	0.02
1a	0[a]	5.53	0.01	8.97	0.01	6.13	0.05	11.95	0.03	5.28	0.02	8.69	0.06
1b		3.90	0.01	6.41	0.02	4.05	0.06	8.24	0.03	2.99	0.10	6.22	0.03
1c		5.62	0.02	9.86	0.03	6.19	0.01	12.46	0.04	5.31	0.03	8.89	0.03
1d		4.73	0.02	9.16	0.02	6.17	0.04	12.33	0.04	4.69	0.02	8.62	0.04
1e		3.08	0.02	5.28	0.03	4.50	0.04	7.60	0.02	2.29	0.04	3.03	0.02

SD: standard deviation; mean values obtained by interpolation at half $\bar{n}$, successive approximation, and mid point methods; [a] logβ values obtained by linear regression analysis

constant and the hydrogen bonding structure of the solvent and is illustrated as follows:

1) Within the alcoholic series (from methanol to 2-propanol), the solvation power decreases and the stability constants of the complexes increase with decreasing dielectric constant [23].

Table 7. logβ_1 and logβ_2 values for Ce^{3+}, Th^{4+}, and UO$_2^{2+}$ chelates with *Schiff* bases **1a–e** in different solvents (70% (v/v) solvent-water)

	Solvent (dielectric)	Ce^{3+}				Th^{4+}				UO$_2^{2+}$			
		logβ_1		logβ_2		logβ_1		logβ_2		logβ_1		logβ_2	
		Mean value	SD	Mean value	SD	Mean value	SD	Mean value	SD	Mean value	SD	Mean value	SD
1a	MeOH	6.82	0.02	13.38	0.02	7.12	0.02	13.81	0.02	6.50	0.02	11.89	0.02
1b	(35.34)	5.50	0.02	10.22	0.02	5.76	0.03	11.11	0.03	5.43	0.03	9.76	0.03
1c		7.22	0.02	13.52	0.02	7.80	0.00	14.93	0.03	6.64	0.00	12.23	0.03
1d		6.89	0.01	12.95	0.02	7.73	0.02	14.72	0.02	6.15	0.02	11.53	0.02
1e		4.55	0.02	8.61	0.02	5.35	0.03	10.25	0.03	4.20	0.03	7.66	0.03
1a	EtOH	7.04	0.02	12.54	0.01	7.30	0.02	14.06	0.02	6.68	0.02	12.55	0.02
1b	(29.13)	5.63	0.02	10.45	0.03	5.85	0.01	11.42	0.02	5.54	0.01	10.17	0.02
1c		7.34	0.02	13.85	0.01	7.98	0.02	15.74	0.02	6.76	0.02	12.66	0.02
1d		7.10	0.02	13.23	0.03	7.88	0.02	15.50	0.03	6.33	0.02	12.07	0.03
1e		4.71	0.02	8.86	0.04	5.64	0.02	10.44	0.02	4.37	0.02	7.84	0.02
1a	1-PrOH	7.22	0.02	13.80	0.01	7.41	0.03	14.23	0.02	6.94	0.03	12.40	0.02
1b	(26.47)	5.79	0.03	10.84	0.03	5.92	0.03	11.42	0.02	5.90	0.03	11.11	0.02
1c		7.54	0.03	14.37	0.04	8.14	0.02	15.80	0.03	7.02	0.02	13.12	0.03
1d		7.40	0.03	13.84	0.02	8.00	0.03	15.42	0.02	6.73	0.03	12.63	0.02
1e		4.89	0.03	9.19	0.02	5.74	0.02	10.92	0.03	4.70	0.02	8.46	0.03
1a	2-PrOH	7.31	0.03	14.12	0.03	7.58	0.02	14.65	0.03	7.12	0.02	13.62	0.03
1b	(24.87)	5.90	0.02	11.20	0.03	6.02	0.01	11.53	0.02	6.06	0.01	11.50	0.02
1c		7.65	0.01	14.79	0.02	8.21	0.02	15.91	0.02	7.39	0.02	13.91	0.02
1d		7.49	0.02	14.50	0.01	8.11	0.02	15.62	0.02	16.97	0.02	12.81	0.02
1e		5.05	0.02	9.44	0.02	5.90	0.01	11.08	0.03	5.01	0.01	9.32	0.03
1a	Acetone	7.89	0.02	14.95	0.04	8.08	0.02	15.84	0.03	7.90	0.02	14.11	0.03
1b	(27.00)	6.31	0.05	11.59	0.03	6.97	0.02	13.21	0.01	6.77	0.02	12.43	0.01
1c		8.16	0.01	15.44	0.03	8.99	0.02	17.22	0.02	8.16	0.02	15.12	0.02
1d		8.00	0.01	15.14	0.03	8.73	0.02	16.84	0.02	7.73	0.02	13.24	0.02
1e		5.48	0.02	10.09	0.02	6.37	0.02	12.12	0.02	6.00	0.02	11.20	0.02
1a	*DMSO*	8.33	0.01	15.55	0.01	8.63	0.02	16.72	0.03	8.36	0.02	14.83	0.03
1b	(12.76)	6.71	0.01	12.35	0.02	7.42	0.02	14.13	0.03	7.10	0.02	13.22	0.03
1c		8.43	0.02	16.11	0.03	9.23	0.03	17.72	0.03	8.62	0.03	16.12	0.03
1d		8.32	0.02	15.92	0.02	9.04	0.04	16.90	0.02	8.02	0.04	14.19	0.02
1e		5.92	0.02	10.77	0.03	6.88	0.22	13.22	0.02	6.30	0.02	11.93	0.02

SD: standard deviation; mean values obtained by interpolation at half $\bar{n}$, successive approximation, and mid point methods

2) Although acetone (20.7) has a dielectric constant higher than 1- and 2-propanol (20.1 and 18.3, respectively), the complexes have higher stability constants in acetone than in the latter solvents. This can be attributed to a decrease in hydrogen bonding structure which assists the complex formation in acetone rather than in 1- and 2-propanol [24] or, in other words, to the smaller solvation capacity of acetone.

Experimental

All chemicals used were of the highest purity available (BDH or Merck products). The solvents were purified according to Ref. [25]; H_2O was distilled twice.

The *Schiff* bases were prepared by condensation of 5,7-dihydroxy-6-formyl-2-methylbenzopyran-4-one [26] with substituted anilines in absolute alcohol for at least one hour except for 4-amino-3-hydroxybenzenesulfonic acid which is insoluble in ethanol. It was dissolved in 4% (w/w) NaOH, and the resulting *Schiff* base was precipitated by acidification to *pH* 2.4 with dilute acetic acid.

10^{-3} *M* $CeCl_3 \cdot 6H_2O$, $Th(NO_3)_4$, and $UO_2(CH_3COO)_2 \cdot 2H_2O$ solutions were prepared and standardized with *EDTA* using the appropriate indicator [27, 28]. Both $CeCl_3 \cdot 6H_2O$ and $Th(NO_3)_4$ were dissolved in water, whereas *Schiff* bases and $UO_2(CH_3COO)_2 \cdot 2H_2O$ were dissolved in ethanol due to their insolubility in H_2O.

Conductometric titrations of 50 ml (4×10^{-5} *M*) *Schiff* base solutions with standard metal ion solutions were carried out using a CM-1K conductivity meter (cell constant: 0.975). Potentiometric titrations were performed applying the *Calvin-Bjerrum pH*-metric titration technique as adopted by *Irving* and *Rossotti* [12, 17] using a digital *pH*-meter (Seibold G103).

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