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APPARENT STABILITY CONSTANTS AND THERMODYNAMIC FUNCTIONS OF CINNAMYLIDENEANILINE SCHIFF BASE COMPLEXES WITH $AlCl_3$

SOBHI K. AL-DILAIMI and A.A. MUTAR

Department of Chemistry, University of Mosul, Mosul (Iraq)

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ABSTRACT

The apparent stability constants and other thermodynamic functions of some $AlCl_3$–cinnamylideneaniline Schiff base complexes in ethanolic solutions have been determined spectrophotometrically. The effects of temperature and substituents on these functions were also studied.

INTRODUCTION

It is well known that different Schiff bases form complexes with various transition metal ions and with some lanthanide ions [1–6], form 1 : 1 complexes with $AlCl_3$ [7], and form a protonated species in dilute mineral acids and glacial acetic acid which absorbs light in the region 440–500 nm [8,9]. The present investigation deals with the electronic and steric effects of the substituents on the availability of the nitrogen lone-pair electron of the azomethine group of the Schiff base in the complex formation with $AlCl_3$. The effect of temperature on the thermodynamic functions of the complex have also been studied.

EXPERIMENTAL

All the Schiff bases used throughout this work were prepared and purified using the procedures described in the literature [10]. Details of the UV–visible instrumentation and calculation of the stability constants have already been reported [7]. The spectrophotometer was connected to an ultrathermostat (Haake NK 22) to control the temperature of the reaction cell.

The standard enthalpy change (ΔH^0) for our Schiff base–$AlCl_3$ complexes was obtained from the apparent stability constant according to eqn. (1), which yielded satisfactory straight lines, then from ΔH^0 other thermody-

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TABLE 1

UV data of several Schiff bases and their complexes with $AlCl_3$

Name	No.	Long λ_{max} in ethanol (nm)	Long λ_{max} for the complex in ethanol (nm)
Cinnamylideneaniline	I	300, 335 [a]	384
Cinnamylidene-*O*-anisidine	II	295, 345	404
Cinnamylidene-*O*-toluidene	III	295, 340 [a]	373
Cinnamylidene-*O*-chloroaniline	IV	300, 340 [a]	396

[a] Shoulder.

namic functions were calculated at a certain temperature.

$$\log K = \frac{-\Delta H^0}{4.576} \frac{1}{T} + \text{constant} \tag{1}$$

RESULTS AND DISCUSSION

The UV spectroscopic data of our Schiff bases and their complexes with $AlCl_3$ are shown in Table 1. The apparent stability constant (K) of the complex decreases monotonically with increasing temperature (Figs. 1 and 2), whereas the free energies (ΔG^0) and entropies (ΔS^0) remain almost constant except for Schiff base IV–$AlCl_3$ complex (Table 2). It is well known that every substituent contributes to one or more of several effects, such as resonance, inductive and steric effects [11], and according to the electron-donating ability of substituents, the stability constants decrease in the order

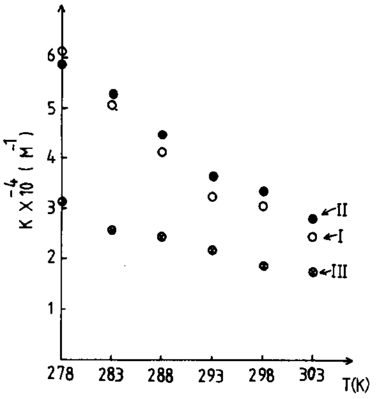

Fig. 1. The effect of temperature on the apparent stability constants of $AlCl_3$ complexes with Schiff bases I, II and III.

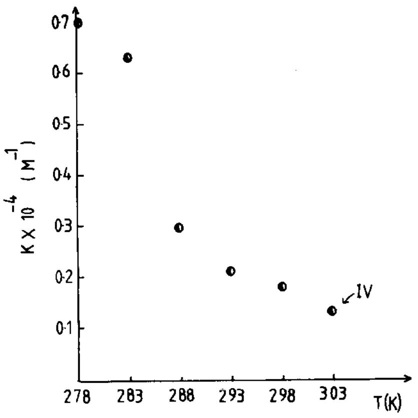

Fig. 2. The effect of temperature on the apparent stabililty constant of $AlCl_3$–Schiff base IV complex.

$OCH_3 > CH_3 > H > Cl$. However, our results indicate that the stability constants follow the order $OCH_3 > H > CH_3 > Cl$, which is probably because the electronic factor seems to play a predominant role, leading to a higher stability constant of the complex of II.

The low stability constant of the complex of III and its high ΔS^0 value suggest that steric hindrance may be exerted by the methyl group during the formation of the complex, which retards the attack of the complexation site by $AlCl_3$. On this basis, it can be concluded that the stability of the complex depends, to a great extend, on the basicity of the azomethine nitrogen or its electronic density [6,4,12].

The negative value of ΔG^0 is in harmony with the observed trend of K, but ΔH^0 is not, and follows the order IV > I > II > III. In compound II, the high value of K should lead to a higher value of ΔH^0 compared with that of I (Table 2), but the reverse was found to be true. This means that ΔH^0 may be affected by the entropy factor; the blocking effect of CH_3O may cause an increase in the entropy as suggested previously [10].

TABLE 2

Values of the thermodynamic functions of the Schiff base–$AlCl_3$ complexes at 278, 283, 288, 293, 298 and 303 K

No.	$-\Delta G^0$ (kJ mol^{-1})	ΔS^0 (J K^{-1} mol^{-1})	$-\Delta H^0$ (kJ mol^{-1})
I	25.45 ± 0.09	0.965 ± 0.176	25.19
II	25.63 ± 0.15	14.29 ± 0.23	21.48
III	24.22 ± 0.29	29.38 ± 0.27	15.68
IV	19.23 ± 1.07	109.5 ± 1.20	51.03

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