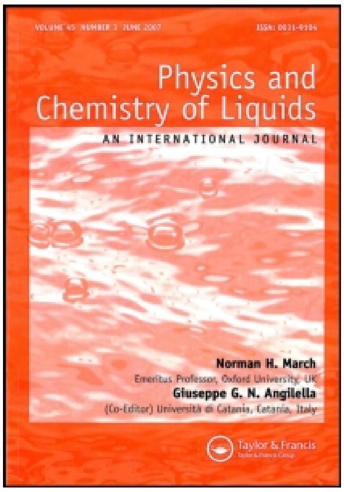

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Interaction of new polyamine ligand *N*,*N*,*N*′, *N*′-tetrakis(2-salicylideneaminoethyl)butane-1,4-diamine with iodine in chloroform and dichloromethane solutions

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The kinetics of complex formation reaction of iodine with *N*,*N*,*N*′,*N*′-tetrakis(2-salicylideneaminoethyl)butane-1,4-diamine have been studied spectrophotometrically at various temperatures in chloroform and dichloromethane solutions. The results indicate the formation of an electron donor–acceptor complex (EDA), which is followed by two relatively slow consecutive reactions. Pseudo-first order rate constants at various temperatures for the formation of the ionic intermediate, and the final product have been evaluated by computer fitting of the absorbance time data to appropriate equations.

Keywords: *N*,*N*,*N*′,*N*′-tetrakis(2-salicylideneaminoethyl)butane-1,4-diamine; Iodine; Rate constant

1. Introduction

Complexation of macrocycles with neutral molecules is a relatively young area of research. Interest in such molecular complexes is strongly stimulated by their possible applications in areas such as separation processes, biomimetic receptors, catalysis of chemical reactions, and conversion of chemical reactions into optical or electronic signals [1]. Such data would be helpful in identifying and understanding reaction driving force and in the characterization of the molecular complexes.

Iodine is a well-known electron-accepting molecule. The charge transfer complexes of iodine with organic molecules have been investigated extensively since the ultraviolet charge transfer absorption band was first reported by Benesi and Hildebrand nearly 50 years ago [2]. Investigations have been performed on complexes in crystals, matrix isolation, neat aromatic solvents, and dilute solutions and in the vapor phase [3–9].

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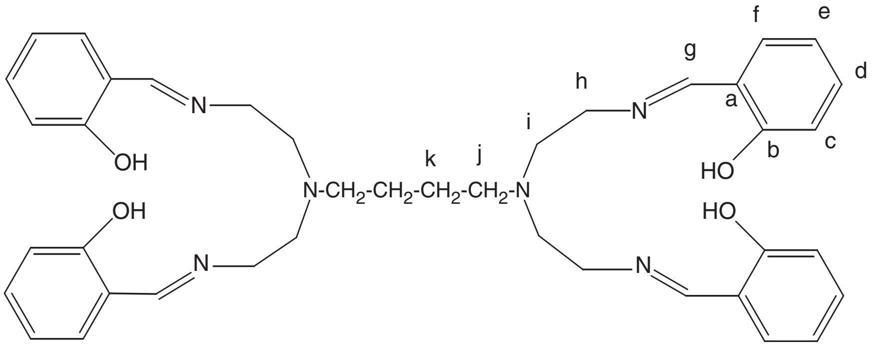

Scheme 1. *N*,*N*,*N*′*N*′-tetrakis(2-salicylideneaminoethyl)butane-1,4-diamine.

In this article, we report the results of a spectrophotometric investigation of the kinetics of the complex formation of a recently synthesized ligand *N*,*N*,*N*′,*N*′-tetrakis(2-salicylideneaminoethyl)butane-1,4-diamine with iodine in chloroform and dichloromethane solutions in different temperatures.

2. Experimental

2.1. *Reagents*

Reagents grade iodine, chloroform, and dichloromethane were obtained from Merck. *N*,*N*,*N*′*N*′-tetrakis(2-salicylideneaminoethyl)butane-1,4-diamine (scheme 1) was prepared and purified according to Ref. [10]. Some of the information of this ligand is:

Anal found: C, 70.85; H, 7.30; N, 12.45; required for $C_{40}H_{48}N_6O_4$: C, 70.98; H, 7.14; N, 12.41%). IR (Nujol); 1637, 1611, 1578, 1284, 1149, 1070, 847, 750, 640 cm^{-1}. ^1H NMR ($CDCl_3$, ppm) δ_H: 13.60 (br s, 4H), 8.15 (s, 4H), 7.26 (td, 4H), 7.02 (dd, 4H), 6.92 (d, 4H), 6.78 (td, 4H), 3.54 (t, 8H), 2.69 (t, 8H), 2.33 (br s, 4H), 1.27 (br s, 4H). ^{13}C NMR ($CDCl_3$, ppm) δ_C: 165.6 (apt ↓), 161.3 (apt ↓), 132.0 (apt ↓), 131.2 (apt ↓), 118.7 (apt ↓), 118.3 (apt ↓), 116.9 (apt ↓), 57.9 (apt ↓), 55.1 (apt ↓), 54.5 (apt ↓), 25.4 (apt ↓).

2.2. *Apparatus*

All UV–Vis spectra and absorbance measurements at different temperatures were carried out on a Shimadzu 265 UV–Visible spectrophotometer with 1 cm quartz cells. At all temperatures, the cell was thermostated with a Shimadzu CPS controller Model 260 to ±0.1°C.

3. Results and discussion

The electronic absorption spectra of iodine ($2.00 \times 10^{-5}\,mol\,L^{-1}$) and synthetic polyamine ligand ($8.00 \times 10^{-5}\,mol\,L^{-1}$) in chloroform solution at 25°C are shown in figure 1. This ligand has a λ_{max} at 325 nm, but iodine does not. Addition of donor to

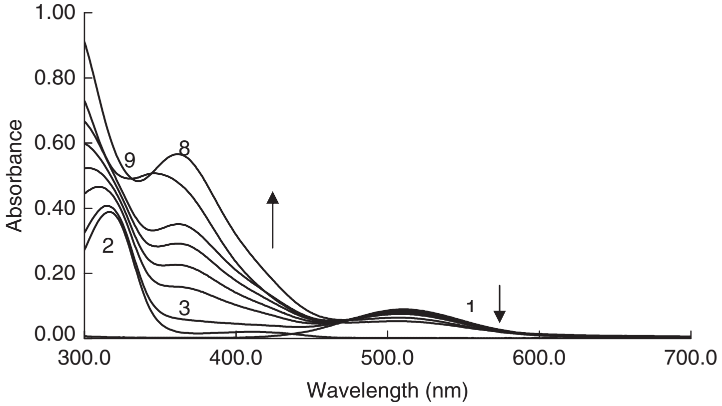

Figure 1. UV–Visible spectra of a mixture of iodine ($2\times10^{-5}\,\mathrm{mol\,L^{-1}}$) and polyamine ligand ($8\times10^{-5}\,\mathrm{mol\,L^{-1}}$) in chloroform solution at 25°C; (1) iodine alone; (2) polyamine alone; (3) immediately after mixing; time intervals: (4) 10 min; (5) 20 min; (6) 30 min; (7) 40 min; (8) 80 min; (9) 6 h.

iodine shows a new absorption band in 370 nm, presumably due to the formation of iodine-ligand complexes. Based on the observed spectral behavior, the formation of the tri-iodide ion can be reasonably assumed to occur in two steps. The first step involves the formation of a molecular complex in the form of $(\mathrm{L}-\mathrm{I}^{+})\mathrm{I}^{-}$ in which the I_3^- ion exists as a contact ion paired anion, i.e.,

$$\mathrm{L} + 2\mathrm{I}_2 \overset{k_1}{\rightleftarrows} (\mathrm{LI}^{+})\mathrm{I}_3^{-} \tag{1}$$

Evidence for the formation of such molecular complexes has been reported previously [11–13]. In the second step, which is actually the rate determining step for the formation of tri-iodide ion, the resulting molecular complex is further decomposed to release free I_3^- ion into solutions. (Solvent separated I_3^-ion).

$$(\mathrm{LI}^{+})\mathrm{I}_3^{-} \overset{k_2}{\rightleftarrows} (\mathrm{LI}^{+}) + \mathrm{I}_3^{-} \tag{2}$$

I_3^- in the contact ion pair has two absorption bands in the 260 and 390 nm regions, but in the solvent separated ion pair these bands shift to 290 and 360 nm, respectively [11–14]. In this study, the ligand shows an absorption band at 325 nm that overlaps with the peak of I_3^- at 290 nm. In the first, the complex shows an absorbance at 370 nm that shifts to 355 nm belonging to the solvent separated ion pair.

The spectra recorded for the EDA complex between ligand and iodine is time dependent. The intensity of the absorption increases with time for about 80 min, however, after a time period of about 80 min the intensity of the absorption band in the 350–380 nm decreases with time. In order to investigate the kinetics of production and consumption of $(\mathrm{LI}^{+})\mathrm{I}_3^{-}$ ion (i.e., k_1 and k_2), the absorbance of a solution with the polyamine ligand : iodine concentration ratio of 10 : 1 ($\mathrm{I}_2 = 5.00\times10^{-6}\,\mathrm{mol\,L^{-1}}$) at different temperatures was monitored at 370 nm in both solvents. Absorbance-time plots for the polyamine ligand $-\mathrm{I}_2$ system in CHCl_3 and $\mathrm{CH}_2\mathrm{Cl}_2$ solutions at different temperatures are shown in figure 2 and 3, respectively.

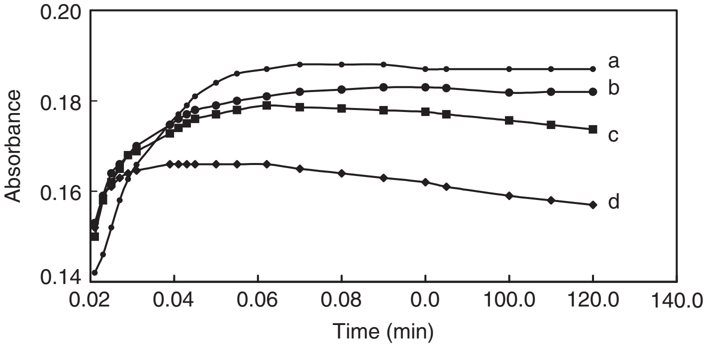

Figure 2. Absorbance-time plots for a mixture of polyamine ligand : iodine = 10 : 1 (concentration of iodine is $5 \times 10^{-6}\,\mathrm{mol\,L^{-1}}$) in chloroform solution at 370 nm at (a) 5°C, (b) 15°C, (c) 20°C and (d) 25°C.

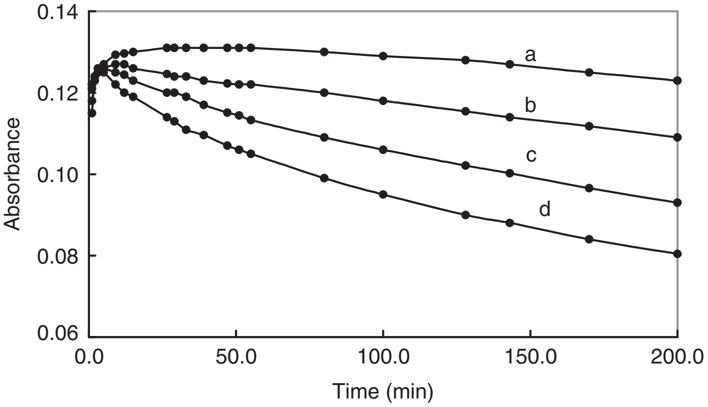

Figure 3. Absorbance-time plots for a mixture of polyamine ligand : iodine = 10 : 1 (concentration of iodine is $5 \times 10^{-6}\,\mathrm{mol\,L^{-1}}$) in dichloromethane solution at 370 nm at (a) 5°C, (b) 15°C, (c) 20°C and (d) 25°C.

For the pair of consecutive reactions given above, the concentrations of species involved as a function of time, under the pseudo-first-order conditions are given by equations [15]:

$$[\mathrm{DA}] = [\mathrm{DA}]_{\mathrm{o}} \exp(-k_1 t) \tag{3}$$

$$[\mathrm{D^+A^-}] = \frac{[\mathrm{DA}]_{\mathrm{o}} k_1 \exp[(-k_2 t) - \exp(-k_1 t)]}{k_1 - k_2} \tag{4}$$

$$[\mathrm{P}] = [\mathrm{DA}]_{\mathrm{o}} \left(\frac{1 + \{[k_2 \exp((-k_1 t) - k_1 \exp(-k_2 t)]\}}{k1 - k2} \right), \tag{5}$$

where $[\mathrm{DA}]_{\mathrm{o}}$ is initial concentration of the EDA complex, and it is assumed that $[\mathrm{D^+A^-}] = [\mathrm{P}] = 0$ when $t = 0$. The absorbance of the reaction solution at time t is given by equation (6), where $\varepsilon_{\mathrm{DA}}$, $\varepsilon_{\mathrm{D^+A^-}}$ and ε_{P} are the molar absorptivities of species DA,

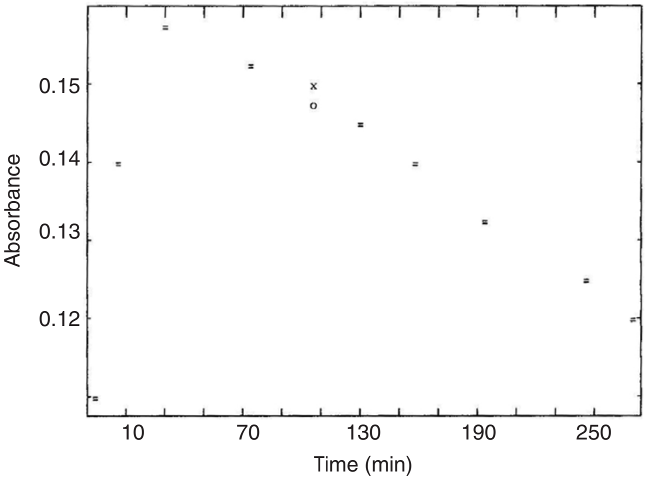

Figure 4. A computer fit of the absorbance-time plot at 5°C. (×): experimental points; (o) calculated points; (=) experimental and calculated points are the same within the resolution of the plots.

D^+A^- and P, respectively.

$$A_t = \varepsilon_{DA}[DA] + \varepsilon_{D^+A^-}[D^+A^-] + \varepsilon_P[P] \tag{6}$$

The substitution of equations (3–5) into (6) and rearrangements results in equation (7).

$$A_t = [DA]_o\left((\varepsilon_{DA} - \varepsilon_P)\exp(-k_{1t}) + \left\{\frac{k_1(\varepsilon_{D^+A^-} - \varepsilon_P \times [\exp(-k_2 t) - \exp(-k_1 t)]}{k1 - k2}\right\} + \varepsilon_P\right) \tag{7}$$

The pseudo-first-order rate constants k_1 and k_2 at various temperatures were then evaluated by fitting equation (7) to a nonlinear least squares curve fitting program KINFIT [16]. The program is based on the iterative adjustment of calculated to observed absorbance values by using either the Wentworth matrix technique [17] or Powell procedure [18]. The adjustable parameters are k_1, k_2, ε_{DA}, and $\varepsilon_{D^+A^-}$, respectively. A sample computer fit of the absorbance-time data is shown in figure 4. A fair agreement between the observed and calculated absorbances further supports the occurrence of the reaction between ligand and I_2 *via* the two-steps mechanism suggested. All the values evaluated for k_1 and k_2 at various temperatures are summarized in table 1. The data given in table 1 indicate that in all cases studied, the pseudo-first order rate constants increase with increasing temperature. The influence of temperature on the k_1 values being much more pronounced than that on the k_2 values.

As the data indicate, the k_1 and k_2 in $CHCl_3$ are lower than CH_2Cl_2 solutions, that means the rate in CH_2Cl_2 are more faster than $CHCl_3$. These behavior may be related to difference in the dielectric constant of two solvents and it is not surprising that in CH_2Cl_2 with $\varepsilon = 9.1$ [19], the intermediate ion pair is less stabilized than in $CHCl_3$ with $\varepsilon = 4.8$.

Activation energies for two reactions were determined from the slopes of the Arrhenius plots lnk *versus* $1/T$.

Table 1. Calculated rate constants and activation energies for iodine and polyamine system in chloroform and dichloromethane solutions at various temperatures.

		Temperature °C					
Solvent	K (min^{-1})[a]	5	10	15	20	25	E_a (kJ mol^{-1})
$CHCl_3$	k_1	$(2.80 \pm 0.18) \times 10^{-2}$	$(6.22 \pm 0.34) \times 10^{-2}$	$(9.89 \pm 0.11) \times 10^{-2}$	$(1.51 \pm 0.38) \times 10^{-1}$	$(2.80 \pm 0.25) \times 10^{-1}$	75.8 ± 2.3
	k_2	$(9.80 \pm 0.51) \times 10^{-8}$	$(1.23 \pm 0.18) \times 10^{-7}$	$(1.65 \pm 0.08) \times 10^{-7}$	$(2.30 \pm 0.31) \times 10^{-7}$	$(3.10 \pm 0.43) \times 10^{-7}$	40.3 ± 3.5
CH_2Cl_2	k_1	0.04 ± 0.01	0.06 ± 0.01	0.08 ± 0.02	0.12 ± 0.02	0.18 ± 0.03	51.0 ± 1.8
	k_2	$(1.86 \pm 0.21) \times 10^{-4}$	$(4.50 \pm 0.17) \times 10^{-4}$	$(1.49 \pm 0.23) \times 10^{-3}$	$(3.50 \pm 0.42) \times 10^{-3}$	$(5.50 \pm 0.31) \times 10^{-3}$	121.9 ± 4.3

[a] Average of three determinations ± SD.

References

[1] R.M. Izatt, J.S. Bradshaw, K. Pawlak, R.L. Bruening, B.J. Tarbet. *Chem. Rev.*, **92**, 1261 (1992).
[2] H.A. Bensi, J.H. Hildebrand. *J. Am. Chem. Soc.*, **71**, 2703 (1949).
[3] R.S. Mulliken, W.B. Pearson. *Molecular Complexes*, Wiley Publishers, New York (1969).
[4] S.D. Christian, J.D. Childs, E.H. Lane. *J. Am. Chem. Soc.*, **94**, 6861 (1972).
[5] M. Hasani, A. Rezaei. *Spectrochim. Acta*, **65A**, 1093 (2006).
[6] B.B. Bhowmik, S.P. Chattopadhyay. *Spectrochim. Acta*, **36A**, 543 (1980).
[7] B.B. Bhowmik, S.P. Chattopadhyay. *Spectrochim. Acta*, **37A**, 135 (1981).
[8] R.A. Sing, S.N. Bhat Can. *J. Chem.*, **59**, 1212 (1981).
[9] J.A. Joens. *J. Org. Chem.*, **54**, 1126 (1989).
[10] H. Khanmohammadi. PhD Thesis, Bu-Ali Sina University, Hamadan, Iran (2004).
[11] A. Semnani, M. Shamsipur. *J. Chem. Soc. Dalton Trans.*, 2215 (1996).
[12] M. Mizuno, J. Tanaka, I. Harada. *J. Phys. Chem.*, **85**, 1789 (1981).
[13] L.J. Andrew, E.S. Prochaska, A. Loewenschuss. *Inorg. Chem.*, **19**, 463 (1980).
[14] R.S. Mulliken. *J. Am. Chem. Soc.*, **74**, 811 (1952).
[15] *Kinetic and Mechanism*, 2nd Edn, p. 166, Wiley, New York (1961).
[16] J.L. Dye, V.A. Nicely. *J. Chem. Educ.*, **48**, 443 (1971).
[17] W.E. Wentworth. *J. Chem. Educ.*, **42**, 162 (1962).
[18] M.J.D. Powell. *Comput. J.*, **7**, 155 (1964).
[19] V. Gutmann. *Coordination Chemistry in Nonaqueous Solvents*, Springer-Verlag, Vienna (1968).