Spectrophotometric Study of the Complexation of Iodine and Bromine with Tetrabutylammonium Halides and Cryptand 222 in Dichloromethane Solution

Semnani, Abolfazl *[+] **and Shareghi, Behzad**
Faculty of Science, Shahrekord University, Shahrekord, P. O. Box 115, I.R. IRAN

Pouretedal, Hamid Reza
Faculty of Science, Malek-Ashtar University of Technology, Shahinshahr, I.R. IRAN

ABSTRACT: *A spectrophotometric study concerning the interactoin between iodine and bromine with tetrabutylammonium iodide (TBAI), tetrabutyl- ammonium bromide (TBABr) and cryptand 222 (C222) has been performed in dichloromethane solution at 25°C. The results are indicative of the formation of* $TBA^+X_3^-$ *and* $C222X^+X_3^-$ *through equilibrium and formation of* $C222X^+X^-$ *through nonequilibrium reactions. The stability constants of the equilibrium reactions were evaluated from the computer fitting of the absorbance-mole ratio data. It was found that iodine complexes were more stable than bromine ones. Comparision of the spectra of* I_2*-TBAI with the* I_2*-C222 mixtures indicates that the isosbestic points of the two systems are not identical. A similar behavior is observed for the corresponding bromine spectra. Comparision of the spectra of iodine complexes with those of bromine also indicates that in the spectra of iodine complexes 1) the wavelength of the isosbestic point is less than* λ_{max} *of the free iodine and 2) addition of C222 or TBAI decreases the absorption intensity at* λ_{max} *of iodine. However, in each case the reverse is observed for the spectra of bromine complexes. The possible reasons for the observed differences in various spectra are explained.*

KEY WORDS: *Cryptand 222, Tetrabutylammonium iodide, Tetrabutyl-ammonium bromide , Spectrophotometry, Iodine, Bromine, Dichloromethane.*

INTRODUCTION

Since the first synthesis of crown ethers [1] and cryptands [2], there has been an intensive amount of research on the thermodynamics and kinetics of complexation of these ligands with various cations in a wide variety of solvent systems [3]. However, the complexation of macrocyclic ligands with neutral

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* To whom correspondence should be addressed.

[+] E-mail : a_semnani@yahoo.com

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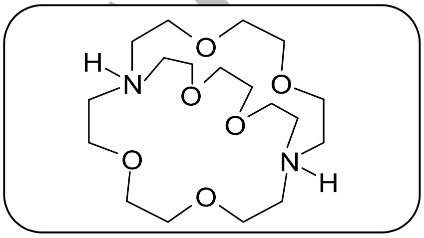
molecules is relatively new in the field of macrocyclic chemistry. Interest in molecular complexes of macrocyclic compounds is strongly stimulated by their possible applications in different areas such as separation processes, biomimetic receptors, catalytic reactions and conversion of chemical energy to optical or electronic signals [4]. Despite the interesting features of macrocycle complexation with neutral molecules, there are few studies in this field [4]. Such studies would be helpful in identifying and understanding the driving forces of reactions and in the characterization of molecular complexes.

We have recently commenced a spectrophotometric study of molecular complexes of crown ethers with different molecules [5-10]. In this paper we report the results of a spectroscopic study of complexation of iodine and bromine with tetrabutylammonium halides and C222 in dichlormethane solution. It must be noticed that there are some simillarity between TBAX-X_2 and C222–X_2 complexes [5-10]. So by comparing the two systems, some special cryptand effects can be determined.

EXPERIMENTAL

C222 from Merck (Darmstadt, Germany) was recrystallized from reagent grade n-hexane and dried under vacuum over P_2O_5.

Reagent grade iodine, bromine, tetrabutyammonium iodide (TBAI), tetrabutylammonium bromide (TBABr) and dichloromethane, all from Merck were of highest purity available and used without any further purification. All UV-Vis spectra were recorded on a Philips PUB700 spectrphotometer and the absorbance measurments were made with a Philips PU875 spectrophotometer at 25±1°C.



C222

RESULTS AND DISUSSION

Iodine complexes

Absorption spectra of 4.73×10^{-5}M of iodine solutions in the presence of increasing quantities of TBAI and C222 are shown in Figs. 1 and 2, respectively. As can be seen, addition of TBAI or C222 to iodine solutions results in two strong absorption maxima at 292 and 364 nm. These bands are well known to be characteristic for the formation of triiodide ion [11-15]. The existence of isosbestic point indicates that this ion is formed through am equilibrium reaction [16]. As the 1:1 (I_2: TBAI) and 2:1 (I_2:C222) stoichiometry of the reactions are confirmed by mole–ratio method (Figs. 3 and 4) [17], the corresponding equations can be written as follows:

$$\mathrm{TBAI}+I_2 \leftrightarrow \mathrm{TBA}^+I_3^- \quad (1)$$

$$\mathrm{C222} + 2I_2 \leftrightarrow \mathrm{C222I}^+.I_3^- \quad (2)$$

To obtain the formation constants of the above molecular complexes, K_f, from the absorbance-mole ratio data, a non-linear least square curve-fitting program KINFIT was used [18]. The program is based on the iterative adjustment of the calculated values of absorbance to the observed values by using either the Wentworth matrix technique [19] or the Powell procedure [20]. Adjustable parameters are K_f and $\in$, where $\in$ is the molar absorptivity of iodine.

The observed absorbance of a solution at the λ_{max} of iodine is given by:

$$A_{obs} = \in b[I_2] \quad (3)$$

The mass balance equation can be written as

$$C_I=[I_2]+[\mathrm{TBA}^+I_3^-] \quad (4A)$$

$$C_I=[I_2]+2[\mathrm{C222I}^+.I_3^-] \quad (4B)$$

$$C_{TBAI}=[\mathrm{TBAI}]+[\mathrm{TBA}^+I_3^-] \quad (5A)$$

$$C_{C222}=[\mathrm{C222}]+[\mathrm{C222I}^+.I_3^-] \quad (5B)$$

The formation constant of the complex is equal to

$$K_f=[\mathrm{TBA}^+I_3^-] / [\mathrm{TBAI}][I_2] \quad (6A)$$

$$K_f=[\mathrm{C222I}^+I^-] / [\mathrm{C222}][I_2] \quad (6B)$$

Substitution of Equations (4) and (5) into Equation (6) and rearrangement yields

$$K_f [I_2]^2+[1+K_f (C_{TBAI}+C_I)[I_2]-C_I=0 \quad (7A)$$

$$K_f [I_2]^3+K_f [2C_{C222}-C_{I2}][I_2]^2+[I_2]-C_{I2}=0 \quad (7B)$$

The free iodine concentration, $[I_2]$ were evaluated from Equation (7) by means of a Newton – Raphson procedure. Once the value of $[I_2]$ has been obtained, the

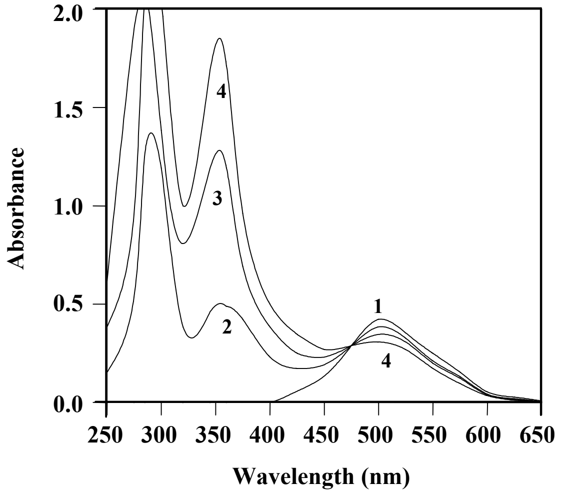


Fig. 1: Absorption spectra of 4.73×10^{-5} M of iodine in dichloromethane in the presence of various concentrations of TBAI. The TBAI: I_2 mole ratios from bottom to the top spectrum are 0.00 , 0.61 , 1.21, 1.83.

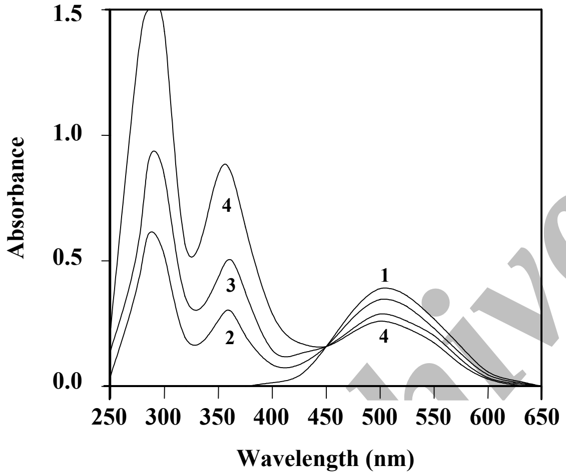


Fig. 2: Absorption spectra of 4.73×10^{-5} M of iodine in dichloromethane in the presence of various concentrations of C222. The C222: I_2 mole ratios from bottom to the top spectrum are 0.00, 0.35, 0.70, 1.04.

corresponding absorbances (A_{cal}), were calculated from the estimated value of ∈ at the current iteration step of the program. Refinement of the parameters is continued until the sum of squares (A_{obs}-A_{cal}) is minimizeid. The output of KINFIT program comprises the refined parameters, the sum-of-squares and the standard deviation of the data. The determined logK_f values by this method for TBAI-I_2 and C222-I_2 complexes were

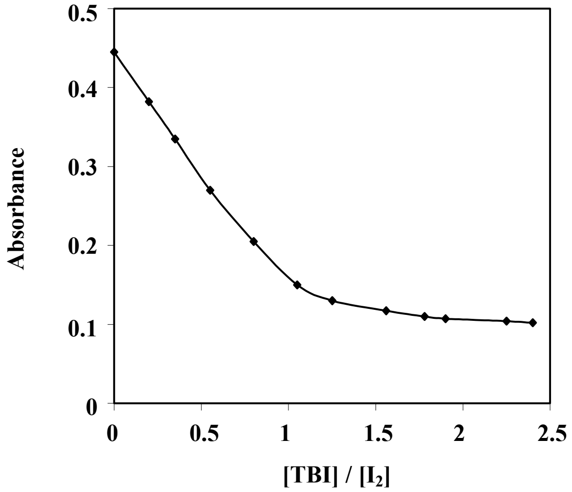


Fig. 3: Plot of absorbance vs. TBAI/I_2 mole ratio in dichloromethane solution obtained at 510 nm and 25°C.

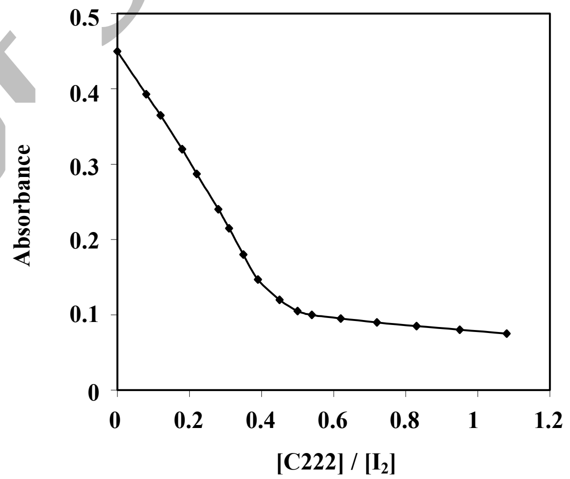


Fig. 4: Plot of absorbance vs. C222/I_2 mole ratio in dichloromthane solution obtained at 510 nm and 25°C.

5.95±0.05 and 6.8±0.12 respectively. A typical curve fitting is shown in Fig. 5.

The spectra of I_2-TBAI mixtures (Fig.1) show that the isosbestic point is located at 474 nm. However the corresponding value for the I_2-C222 mixtures is 450 nm. The difference in isosbestic points can be attributed to the difference in ∈ values of $TBA^+I_3^-$ and $C222I^+I_3^-$ [16]. The difference also originates from the various effects of TBA^+ and $C222I^+$ on the absorption intensity of I_3^- ion. It must be noticed that TBAI and C222 do not have any absorption in the visible region and I_2 is common in both systems (Equations 1 and 2).

It is interesting to note that the addition of excess C222 to the yellow solution of $C222I^+. I_3^-$ will result in its fading. In contrast the TBAI-I_2 system does not show such a behaviour; i.e. in the presence of excess TBAI the yellow color of $TBA^+I_3^-$ does not change. It seems that macrocyclic effect as well as soft–soft interactions [21-24] play important roles in these different behaviors. In fact the strong tendecy of C222 for inclusion of I^+ acts as a strong driving force. This force causes the conversion of I_3^- to I^+ and I^- through the following disproporation reaction.

$$C222I^+I_3^-(\text{yellow})+C222 \leftrightarrow 2C222I^+I^-(\text{colorless}) \qquad (8)$$

Both I^+ and I^- do not show any considerable absorption in the visible region [5-10] . So the above reaction has a colorless product.

Keeping in mind that TBAI does not have any special effect on the $TBA^+I_3^-$, we could not observe any reaction between TBAI and $TBA^+I_3^-$. Consequently no color change is observed in the presence of excess TBAI.

Bromine complexes

The existence of an isosbestic point in the absorption spectra of TBABr-Br_2 mixtures (Fig. 6) proves the presence of an equilibrium reaction between the components. The 1:1 stoichiometry of the reaction is confirmed by the mole ratio method (Fig. 7). So the interaction between TBABr and Br_2 can be shown by the following chemical equation:

$$TBABr+Br_2 \leftrightarrow TBA^+Br_3^- \qquad (9)$$

The equilibrium constant of the above reaction was also evaluated by computer fitting of the absorbance - mole ratio data. The value determined was 5.5±0.01 .

Absorption spectra of 2.42×10^{-3} M bromine solution in the presence of increasing quantities of C222 are shown in Fig. 8. As can be seen, the initial part of the spectra are simillar to that of TBABr-Br_2 mixtures. So it can be concluded that the two systems have the same product and in both systems Br_3^- is formed through the following equilibrium reactions:

$$TBABr + Br_2 \leftrightarrow TBA^+Br_3^- \qquad (9)$$

$$C222 + 2Br_2 \leftrightarrow C222Br^+Br_3^- \qquad (10)$$

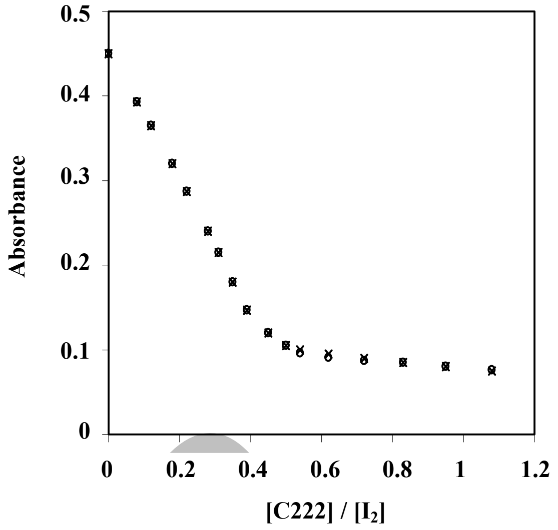


Fig. 5: Computer fit of the absorbance vs. C222/I_2 in dichloromethane obstained at 510nm and 25°C: (x) experimental point; (o) calculated Point

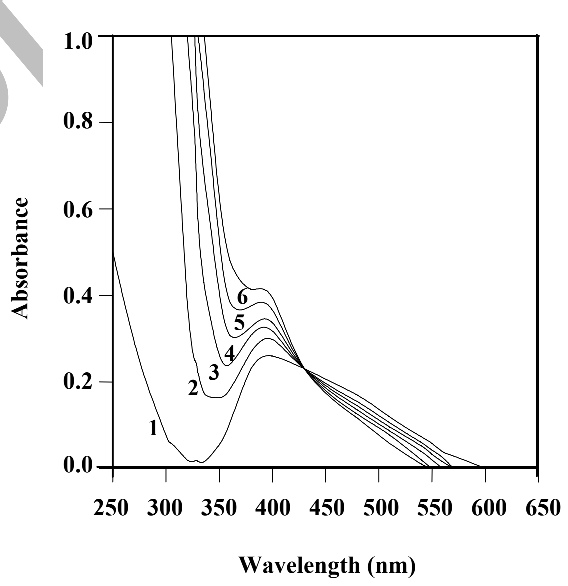


Fig. 6: Absorption spectra of 2.42×10^{-3} M of bromine in dichloromethane in the presence of various concentration of TBABr. The TBABr: Br_2 mole ratios from bottom to the top are: 0.00, 0.03, 0.05, 0.08, 0.11, 0.13.

However, at higher concentrations of C222, not only the isosbestic point is broken, but also the spectra shift to the UV region and the solution color fades. This means that at high C222/Br_2 mole ratio, a new nonequilibrium

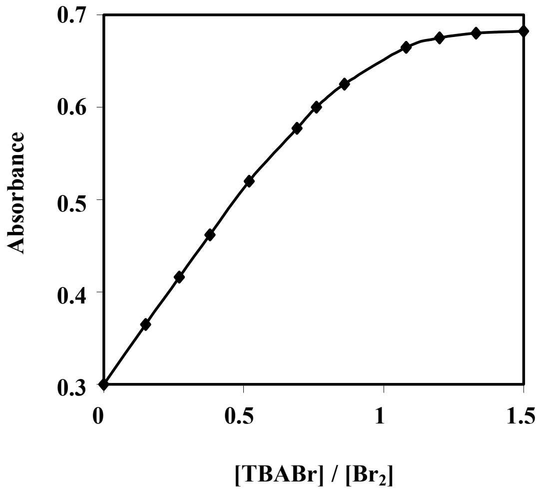


Fig. 7: Plot of absorbance vs. TBABr/Br_2 in dichloromethane solution obtained at 405 nm and 25°C

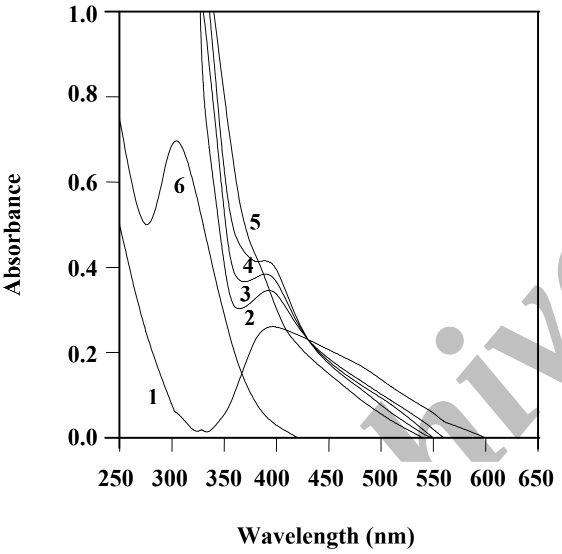


Fig. 8: Absorption spectra of 2.42×10^{-3} M of bromine in dichlromethane in the presence of various concentrations of C222: 1, 0.00M; 2, 2.42×10^{-4}M; 3, 4.84×10^{-4}M; 4, 7.26×10^{-4}M; 5, 2.42×10^{-3}M; 6, 2.9×10^{-3}M;.

reaction occurs. The color fading is indicative of formation of a colorless product. Taking in to account that $C222Br^+Br^-$ is the most probable colorless adduct,the following reaction can be written.

$C222Br^+Br_3^-$(brown)+C222↔$2C222Br^+Br^-$(colorless)(11)

Absorbance–mole ratio plot (Fig.9) shows that the above reaction occurs at C222/Br_2 mole ratios of more

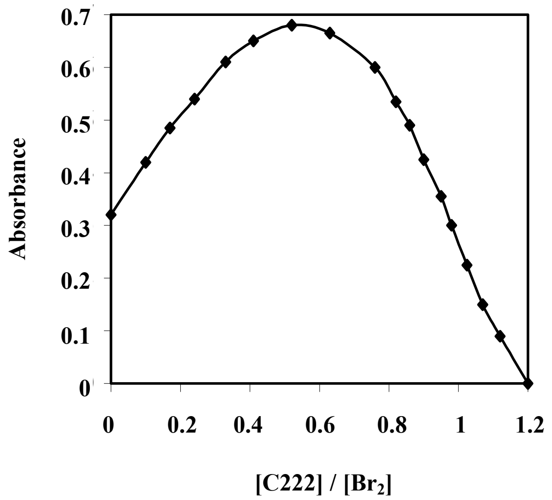


Fig. 9: Plot of absorbance vs. C222/Br_2 in dichloromethane solution obtained at 405 nm.

than 0.5. An estimated value of logK_f was obtained by fitting the first part of the recent curve. The value obtained was 6.1±0.4 .

The isosbestic points of TBABr- Br_2 and C222–Br_2 spectra are located at 424 and 432 nm, respectively. Similar to I_2 complexes, the difference can be attributed to the various effects of TBA^+ and $C222Br^+$ on the absorption intensity of Br_3^- ion.

CONCLUSIONS

The final thermodynamic and spectroscopic results are presented in Table 1. According to the data and the previous discussion it can be concluded that:

1) In all systems the following equilibria exists.

$C222$ (or TBAX)+$2X_2$ (or X_2)↔$C222X^+$(or TBA^+)X_3 (12)

2) The stability of iodine complexes are more than bromine ones. This can be attributed to lower electronegativity and higher donocity of iodine relative to bromine

3) As a result of macrocyclic effect and soft–soft interactions, the excecs C222 causes the following reaction to occur.

$C222+C222X^+X_3^- \leftrightarrow 2C222X^+X^-$ (13)

Due to lack of any special effect in the presence of excess TBAX, a similar reaction does not occur in this case.

$TBAX + TBA^+X_3^- \leftrightarrow$ no reaction (14)

Table 1: Spectral and thermodynamic data of iodine and bromine complexes

System	$^a\lambda_{max}$	$^b\lambda'_{max}$	$^c\lambda_{IP}$	Stoichiometry	Log K_f
TBAI-I_2	510	290-364	474	1:1	5.95±0.05
C222-I_2	510	290-364	450	2:1	6.8±0.12
TBABr-Br_2	405	-	424	1:1	5.5±0.01
C222-Br_2	405	-	432	2:1	6.1±0.4

a) The maximum wavelength of iodine and bromine in the absence of complexing agents
b) The absorption maximum of resulting complexes
c) The wavelength of isosbestic point

4) TBA^+ and $C222X^+$ have different effects on molar absorption coefficient of X_3^-. So in the spectra of both the bromine and iodine complexes, the wavelengths of isosbestic points of TBAX-X_2 and C222-X_2 systems are not identical.

5) In the spectra of the bromine complexes the wavelength of isosbestic points are higher than λ_{max} of free bromine. Also in the presence of TBABr or C222 (Figs. 6 and 8) the absorption intensity at λ_{max} of bromine increases. However the reverse is observed for iodine complexes (Figs. 1 and 2). It seems that such a different behaviour originates from the different kind of transitions in the two systems. In bromine complexes the charge transfer transitions, result in wide bands. The overlap of these bands with bromine spectrum, causes an increase in the absorption intensity at λ_{max} of bromine and location of isosbestic point wavelangth (λ_{IP}) at wavelengths higher than λ_{max} of the free bromine. But in iodine complexes the charge transfer bands are not wide and the reverse effect is observed.

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REFERENCES

[1] Pederson, C. J., *J. Am. Chem. Soc.*, **89**, 7017 (1967).

[2] Dietrich, B., Lehn, J.M. and Sauvage, J.P., *Tetrahedron Lett.*, 2885 (1969).

[3] Izatt, R. M., Pawlak, K., Bradshaw, J. S. and Bruening, R. L., *Chem. Rev.*, **91**, 1721 (1991).

[4] Izatt, R.M., Bradshaw, J. S., Pawlak, K., Bruening,R. L. and Tarbet, B. J., *Chem. Rev.*, **92**, 1261 (1992).

[5] Semnani, A. and Shamsipur, M., *Spectrochim Acta*, **49 (A)**, 44 (1993).

[6] Semnani, A. and Shamsipur, M., *Journal of Inclusion Phenom.*, **22**, 99 (1995).

[7] Semnani, A. and Shamsipur, M., *J. Chem. Soc. Dalton Trans*, 2215 (1996).

[8] Semnani, A. and Shamsipur, M., *Polish J. Chem.*, **95**, 134 (1997).

[9] Semnani, A., Shareghi, B. and Sovizi, M., *Iran. J. Chem. & Chem. Eng.*, **19**, 67 (2000).

[10] Semnani, A. and Shareghi, B., Proceeding of 18th Phillippine Chemistry Congress, Phillippines, 19-23 Feb. (2002).

[11] Hopkins, H. P., Jahagirdar, D. V. and Windler, F., *J. Phys. Chem.*, **82**, 1254 (1978).

[12] Nour, E. M. and Shahada, L. A., *Spectrochim. Acta*, **44 (A)**, 1277 (1988).

[13] Hirsch, W., Greenman, J. and Pizer, R., *Can. J. Chem.*, **71**, 2171 (1993).

[14] Lang., R. P., *J. Phys. Chem.*, **78**, 1657 (1974).

[15] Mizuno, M., Tanaka, J. and Harad, I., *J. Phys. Chem.*, **85**, 1789 (1981).

[16] Christian, G.D. and O'Reilly, J.E, "Instrumental Analysis", Sec. Ed. Allyn and Bacon (1986).

[17] Beck, M.T. and Nagypal, I., "Chemistry of Complex Equilibria "John Wiely & Sons (1990).

[18] Nicely, V. A. and Dye, J. L., *J. Chem. Educ.* **48**, 443 (1971).

[19] Wentworth, W. E., *J. Chem. Educ.*, **42**, 69 (1962).

[20] Powell, M. J. D., *Comput. J.*, **7**, 155 (1964).

[21] Pearson, R. G., *Struct. Bonding (Berlin)*, **2**, 80 (1993).

[22] Semnani, A. and Hemmat, M., *Iran. J. Sci. & Tech.*, **26**, 7 (2002).

[23] Parham, H. and Shamsipur, M., *Talanta*, **40**, 1353 (1993).

[24] Parham, H. and Shamsipur, M., *Sep. Sci. Technol.*, **30**, 3061 (1995).