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Studies of Molecular Complexes of Some Π Donors with Iodine by Constant Activity Method

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The iodine complexes of benzene, toluene, *o*-, *m*-, *p*-xylene and mesitylenes in cyclohexane are studied by using constant activity method. The association constants and the other thermodynamic parameters of the complexes are determined and the results are compared with those obtained by using conventional spectral methods. The blue shifted iodine band maxima are determined directly.

Although extensive spectrophotometric studies have been made on molecular complexes of iodine with various electron donors, reliable informations are still lacking on thermodynamic and spectral constants, particularly for weak donor–iodine complexes.[1–4] The constant activity method proposed by Childs *et al.*,[5] allows precise determination of the position as well as molar extinction coefficient of the blue-shifted iodine band, ε_{BS}, directly. So recently we have begun the investigations of a number of electron donor–acceptor complexes of iodine by the constant activity method, some of which were studied by the earlier investigators by spectral methods, but whose importance as typical examples is so great that extra efforts to obtain accurate data are justified.[6–7] In the present paper, the studies of iodine complexes of weak donors, namely benzene, toluene, xylenes, and mesitylene by constant activity method, have been reported.

Materials and Method

Solid tetramethylammonium pentaiodide ($TMAI_5$) was prepared as described by Chattaway and Hoyle.[8] All the donors namely benzene, toluene, xylenes, and mesitylene and acceptor, iodine, were purified by the standard procedures. Purified cyclohexane was used as solvent.

The procedure used to obtain the equilibrium constant, K_c, is based on using a mixture of tetramethylammonium polyoidides to maintain a constant activity of iodine, *e.g.*,

$$(CH_3)_4NI_5(s) \rightleftharpoons (CH_3)_4NI_3(s) + I_2.$$

The concentration of iodine is controlled by the temperature of the experiment. Addition of a donor to this system establishes a second equilibrium between donor and iodine,

$$D + I_2 \rightleftharpoons DI_2.$$

The latter equilibrium can be analyzed directly from the increase in absorbance at the isosbestic point of iodine in visible region and the procedure used to obtain the equilibrium constant, K_c, has been described in detail elsewhere.[6,7]

For obtaining isosbestic point, as well as the molar extinction coefficient at the isosbestic point, ε_{isos}, the spectra of pure iodine and complexed iodine in cyclohexane were recorded by keeping the iodine concentration constant (≈0.4 mM†) and varying the donor concentration (1—5 M). Pure $TMAI_5$ was equilibrated with cyclohexane (≈48 h) at constant temperature (in a thermostat) and the spectrum of iodine in the equilibrium solution was recorded. Then a series of several solutions of donors in cyclohexane were similarly equilibrated with $TMAI_5$ (≈150 mg) and spectra were recorded for all those solutions at all constant temperatures.

The spectra were recorded in UV and visible region by Beckmann 26 recording spectrophotometer fitted with a temperature control accessories with a four position manual sample changer. The spectra were recorded at 25, 30, 35, and 40 °C and the temperature of the solution could be controlled within ±0.1 °C. However, for the sake of brievity, the data at only one temperature have been reported.

For locating the blue-shifted iodine band of the donor–iodine complex, the spectrum of the complex was recorded with the donor and the constant activity source of iodine in the sample cell and only the constant activity source of iodine in the reference cell, at constant temperature.

Results and Discussion

Benzene–Iodine System. Figure 1 shows the iso-

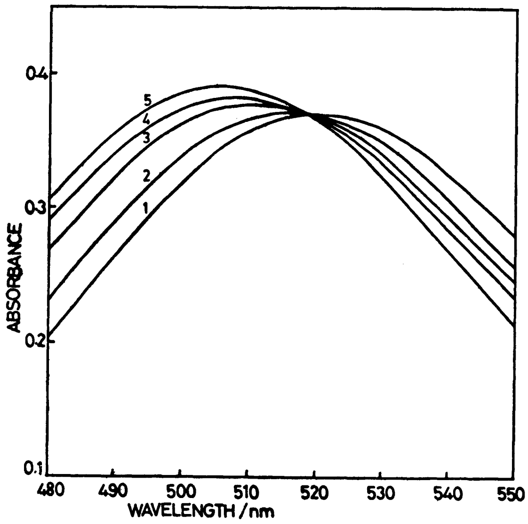

Fig. 1. Isosbestic point of the benzene-iodine complex in cyclohexane at 25 °C, cell path = 1.00 cm.
(1) Iodine alone (4.0×10^{-4} M); (2) I_2 + 1 M benzene; (3) I_2 + 2 M benzene; (4) I_2 + 3 M benzene; (5) I_2 + 4 M benzene.

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† 1 M = 1 mol dm^{-3}.

sbestic point of benzene–iodine complex (at 518 nm). The molar extinction coefficient of iodine in cyclohexane at 518 nm is 962 dm³ mol⁻¹ cm⁻¹ (Table 1). The isosbestic point does not vary with the concentration of the donor (in the experimental range of concentration of 1 M to 5 M) and the increase in absorbance at the isosbestic point is attributed solely to the formation of the complex. The charge-transfer band appears at 298 nm (Table 2). The equilibrium constants were determined at 25, 30, 35, and 40 °C, but K_c value at only one temperature, *i.e.*, 25 °C has been listed for the sake of brievity (Table 3). Our data agree with those of Plucknett[9] as well as of Childs *et al.*,[5] but differ from those of Keefer[10]. The K_c values obtained by constant activity method *i.e.* K_c^s are generally higher than those obtained by conventional spectral method using Benesi-Hildebrand[11] procedure. The discrepancy is more in weak complexes. In the case of strong complexes like pyridine–iodine, the contribution due to nonspecific interaction between the donor and iodine is around zero and under such circumstances K_c^s will be equal to K^{th} (*i.e.*, corrected equilibrium constant[4,12]). Moreover, the activity coefficient, γ, varies throughout the range of donor concentration and the values of association constant corrected for γ_{I_2} estimated from solubility parameters are comparable to those reported, obtained by B-H method[12]. Trotter and Hanna[13] had suggested a simple model. According to them a molecule of D replaces one of the molecules in the solvent shell surrounding A, and the equilibrium constant is given by

$$K_{exp} = K^* - [S]_0^{-1},$$

where $[S]_0^{-1}$ is the molar volume of the pure solvent and K^* is the true association constant (corresponding to the equilibrium $AS_n + DS_m \rightleftharpoons \overline{ADSP} + qS$). Applying the correction due to this, the corrected values are given in Table 3. Here it must be worth mentioning that the literature data correspond to heptane (as solvent) and our data correspond to cyclohexane. If one carefully goes through the literature data, one finds that $K_{heptane} > K_{cyclohexane}$.

The concentrations of benzene used for obtaining equilibrium constants are from 0.25 M to 1.5 M. We observed ΔA_{CT} (the change in A_{CT}—Absorbence at the charge-transfer band corrected for free iodine band and donor) varies reasonably linearly with ΔA_{isos}, and the linear regression line forced through the origin is used to calculate the limiting slope of the plot. The molar absorptivity of the charge-transfer band is 9450

TABLE 1. MOLAR EXTINCTION COEFFICIENT AND ISOSBESTIC POINTS OF IODINE COMPLEXES IN CYCLOHEXANE AT 298 K

[I] = 4.0 × 10⁻⁴ M; path length = 1.00 cm, [D] = 1.0 to 5 M.

Donor	λ^*_{isos} nm	A_{isos}	ε^{**}_{isos} dm³ mol⁻¹ cm⁻¹
Benzene	518 (520)[a]	0.385	962
Toluene	515 (518)[a]	0.383	959
o-Xylene	519 (519)[a]	0.388	971
m-Xylene	518 (518)[a]	0.389	973
p-Xylene	518 (518)[a]	0.392	980
Mesitylene	519 (520)	0.392	980

* ±1 nm, ** ±2.5. a) Childs Ph. D. thesis, Univ. of Oklahoma (Normon, Oklahoma, 1971) as quoted by M. Tamres in "Spectroscopy and Structure of Molecular Complexes".

TABLE 2. SPECTRAL CHARACTERISTICS OF CHARGE-TRANSFER AND VISIBLE BANDS OF SOME IODINE COMPLEXES

Solvent: cyclohexane, temp = 298 K.

Donor	I_D/eV	Charge-transfer band					Visible band				
		$\lambda_{CT}^{b)}$ nm	$\varepsilon_{CT}^{c)}$ dm³ mol⁻¹ cm⁻¹	$\Delta\bar{\nu}_{1/2}^{d)}$ cm⁻¹	$f^{e)}$	$\vec{\mu} \times 10^{30}$ C m	λ_{max}^* nm	$\varepsilon_{max}^{c)}$ dm³ mol⁻¹ cm⁻¹	$\Delta\bar{\nu}_{1/2}^{d)}$ cm⁻¹	$f^{e)}$	$\vec{\mu} \times 10^{30}$ C m
Benzene	9.254	289 (288)[a]	9450 (8080)[a]	5042	0.206 (0.280)[g]	11.8 (13.7)[g]	503 (504)[a]	1023 (984)[a]	3067 (3320)[a]	0.0135 (0.0142)[a]	4.01 (4.13)[a]
Toluene	8.82	301 (300)[a]	9472 (6900)[a]	6231	0.259	13.6	500 (502)[a]	1039 (1020)[a]	4126 (3240)[a]	0.0185 (0.0143)[a]	4.67 (4.13)[a]
o-Xylene	8.56	313 (313)[a]	8570 (6520)[a]	6230	0.231	13.1	500 (501)[a]	1093 (1030)[a]	3558 (3450)[a]	0.0168 (0.0153)[a]	4.44 (4.26)[a]
m-Xylene	8.50	314 (314)[a]	8193 (5719)[a]	6390	0.226	12.9	497 (499)[a]	1102 (1030)[a]	3316 (3430)[a]	0.0158 (0.0158)[a]	4.30 (4.30)[a]
p-Xylene	8.445	303 (303)[a]	7733 (6550)[a]	9718	0.324	15.24	500 (501)[a]	1088 (1060)[a]	3414 (3460)[a]	0.0160 (0.0153)[a]	4.35 (4.26)[a]
Mesitylene	8.40	329 (327)	9000 (7730)	9002	0.350	16.49	496 (495)[a]	1130 (1110)[a]	3500 (3470)[a]	0.0170 (0.0169)[a]	4.47

a) J. D. Childs, Ph. D. thesis, University of Oklahoma (Normen, Oklahoma, 1971), as reported by M. Tamres in "Spectroscopy and Structure of Molecular Complexes." b) ±1 nm. c) Average error limit = ±100; C: average error limit = ±50. d) Half width, difference in wave number at half the maximum intensity on the high and low energy side of the band, ±40 cm⁻¹. e) Oscillator strength calculated from, $f = 4.42 \times 10^{-9}$. $\varepsilon_{max} \cdot \Delta\bar{\nu}_{1/2}$ ±0.0025. f) Transition moment, calculated from, $\vec{\mu} = 0.0958\left[\frac{\varepsilon_{max} \cdot \Delta\bar{\nu}_{1/2}}{\bar{\nu}_{max}}\right]$. g) B. B. Bhowmik., *Spectrochim. Acta, Part A*, **27**, 321 (1971). *: ±2 nm.

TABLE 3. SUMMARY OF THE THERMODYNAMIC PARAMETERS OF SOME COMPLEXES OF IODINE
Solvent: cyclohexane, temp: 298 K.

Donor	K_c[b]	ε_{CT}[c]	$-\Delta H°$[d]	$-\Delta S°$
	$dm^3 mol^{-1}$	$dm^3 mol^{-1} cm^{-1}$	$kJ mol^{-1}$	$J mol^{-1}$
Benzene	0.365 (0.356)[a] (0.348)[h]	9450 (8080)[a]	6.65 (6.78)[e]	30.75 (34.1)[e]
Toluene	0.409 (0.500)[a] (0.382)[h]	9472 (6900)[a]	8.69 (7.5)[f]	36.29 (35.5)[f]
o-Xylene	0.658 (0.641)[a] (0.640)[h]	8570 (6520)[a]	8.75	32.8 (36.0)
m-Xylene	0.730 (0.698)[a] (0.705)[h]	8193 (5910)[a]	8.00	29.51
p-Xylene	0.725 (0.642)[a] (0.700)[h]	7733 (6550)[a]	10.10 (9.12)[g]	47.23 (40.2)[g]
Mesitylene	0.962 (0.960) (0.955)[h]	9000 (7730)[a]	12.00	41.41 (44.7)

a) Childs, Ph. D. Thesis, Univ. of Oklahoma (Norman, Oklahoma, 1971) as reported by M. Tamres, in "Spectroscopy and Molecular Structure." b) ±0.005; c) ±100; d) ±0.06. e) Ref. B. B. Bhowmik, *Spectrochim. Acta, Part A*, **27**, 321 (1971); f) Ref. J. A. A. Ketelaar, *J. Phys. Rad. (Paris)*, **15**, 197 (1954). g) Andrews and Keefer, *J. Am. Chem. Soc.*, **74**, 4500 (1952). Keefer and Andrews, *ibid.*, **77**, 2161 (1955); h) Calculated by using Trotter and Hanna's method. Ref. 13.

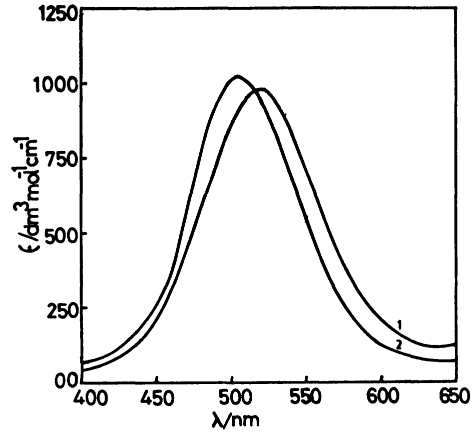

Fig. 2. Visible spectra of benzene–iodine complex in cyclohexane by constant activity method at 25 °C. 1. Free iodine; 2. complexed iodine.

±100 $dm^3 mol^{-1} cm^{-1}$ which is higher than the reported value. (As the intensity of a CT transition is best measured by its oscillator strength, *f*, or its transition dipole moment, μ_{VN}, the results for alkyl benzenes –iodine complexes are summarised in Table 2) As we do not have any informations regarding the experimental conditions of Childs *et al.*[5] we are unable to comment on this. However, it is worth mentioning that Orgel and Mulliken[14] are of the opinion that approximately, one fourth of the CT band intensity for benzene–iodine interaction in CCl_4 is due to absorption by complex and the remaining results from "donor–acceptor contacts" due to which the molar absorptivity is high. Lane *et al.*,[12] have rightly pointed out in the case of weak molecular complexes (when the donor concentration is high), the value of ε determined using different concentration scales can differ widely (due to $d\gamma_i^{\dagger}/dC_D \neq 0$). The molar absorptivity of the complex appears to decrease with the increase in temperature which may be due to band broadening.[2,4] The enthalpy, $-\Delta H°$ (6.65 $kJ mol^{-1}$), agrees well with the literature value. The heats of complexation must be considered as representing a composite results for benzene–iodine of different aggregation.

The visible spectrum of iodine–benzene system in cyclohexane obtained by the constant activity method has been shown in Fig. 2. The blue-shifted iodine band maximum (λ_{BS}) is at 503±2.0 nm (Table 2). An examination of the spectra at different concentrations of benzene (0.1 M to 1.5 M) shows that the blue-shifted iodine band position slightly shifts to lower wavelengths with the increase in concentration of donor. However, the shift is within the experimental error. Similar observations were made recently for benzene–iodine system from supersonic beam method.[15] Voigt[16] has reported that iodine absorbs at 502 nm in benzene. This change in λ_{BS} (with concentration), may be due to specific and non-specific interaction of iodine with the medium. The so called dielectric theory may successfully correlate the solvent shift of the absorption band to the dielectric media. As the dielectric constant is increased, (concentration of benzene is increased), the absorbance energy increases, *i.e.*, there is a blue shift in the absorption medium.

The "blue-shift" of iodine band in polar media is due to perturbation of I_2 by its complexing partner.[1] The B←X electronic transition in I_2 shifts an electron from a π_g to a σ_u antibonding orbital which is spacially larger. So the magnitude of the iodine blue shift should correlate well with the electron donor ability of the bonding solvent molecules. The molar absorptivity of the blue shifted iodine band maximum, ε_{BS}, is 1023±50 $dm^3 M^{-1} cm^{-1}$. The characteristic intensification of the shifted iodine band is explained by increased mixing of the $^3\pi_{0+u}$ state (520 nm band) with either CT the state or with the other excited states (like $^1\Sigma_u^+$ state). The shift and mixing should be greater the stronger the complex, leading to a greater borrowing intensity and therefore a more intense band.[1] The oscillator strength and the transition dipole moments for the blue shifted iodine band are reported in Table 2.

Toluene–Iodine System. The isosbestic point, charge-transfer band, blue-shifted iodine band and the molar extinction coefficients of toluene–iodine system are given in Tables 1—3. It can be seen from the data that the average equilibrium constant at 25 °C is 0.409 $dm^3 mol^{-1}$ and it is slightly lower than the literature value of 0.500 $dm^3 mol^{-1}$. The enthalpy is higher than that of benzene–iodine complex which is expected. The molar extinction coefficient of toluene–

iodine complex at CT band (310 nm) is slightly lower than that of benzene–iodine which is not expected (provided the structures are the same). Such discrepancy was reported earlier also. Murakami[17] is of the opinion that since "the degree" of overlapping between orbital functuons which are essential to CT interactions is considerably different for different models, it is reasonable to assume that each configuration has its own molar extinction coefficient. The oscillator strength and transition dipole moments of toluene–iodine are higher compared to those of benzene–iodine complex, which is expected. The blue-shifted iodine band maximum which is slightly concentration dependent of the donor for toluene–iodine appears at 500 nm ($\varepsilon_{BS}=1039$ dm^3 mol^{-1} cm^{-1}). This observation of λ_{BS}, ε_{BS}, f and μ_{VN} data (Table 2) indicate that toluene–iodine is definitely a stronger complex compared to benzene–iodine.

Xylenes–Iodine System. The isosbestic points, charge-transfer bands, blue-shifted iodine bands and their molar extinction coefficients of *o*-, *m*-, and *p*-xylene–iodine complexes are summarised in Tables 1—3. The molar extinction coefficients of the charge-transfer bands are higher than those compiled by Tamres.[18] (In the absence of detailed information in the literature we are not in a position to comment on this) The oscillator strengths and transition dipole moments of CT band indicate that *p*-xylene–iodine complex seems to be stronger compared to the others. These go in parallel with the ionization potentials of the donors. The molar extinction coeffecients, the oscillator strengths and transition dipole moments of visible bands are nearly the same (Table 2). So it is not possible to compare the strength of xylene–iodine complexes from visible absorption band data.

Mesitylene–Iodine System. The spectral and thermodynamic parameters of mesitylene–iodine complexes are reported in Table 1—3. Judging from the position of blue-shifted band and equilibrium constant and other thermodynamic parameters, it is clear that mesitylene–iodine complex is stronger compared to benzene–iodine or xylenes–iodine complexes.

Thus, as shown earlier, our present observations confirm our earlier suggestive evidences that the constant activity method (sometimes known as polyiodide solubility method or simply solubility method) is a convenient alternative to purely spectral methods for determining K_c and ε_{CT} especially for weak molecular complexes of iodine. Secondly the blue shifted iodine band maximum can be obtained precisely and directly. In addition to this, the heat of complexation can be determined by temperature dependence study of the absorbance of the complex using only a single solution of donor with excess of polyiodide.

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References

1) R. S. Mulliken and W. B. Person, "Molecular Complexes", Wiley Interscience, New York (1969).

2) "Molecular Complexes," ed by R. Foster, Eleck Science, London (1974), Vols. I and II.

3) C. N. R. Rao, S. N. Bhat, and P. C. Dwivedi, *Appl. Spectros. Revs.*, **5**, 1 (1972).

4) M. Tamres "Spectroscopy and Structure of Molecular Complexes," ed by J. Yarwood, Plenum Press, London (1973).

5) a) J. D. Childs, S. D. Christian, J. Grundness, and S. R. Roach, *Acta Chem. Scand.*, **25**, 1679 (1969); b) J. D. Childs, S. D. Christian, and J. Grundness, *J. Am. Chem. Soc.*, **94**, 5657 (1972).

6) J. Grundness, M. Tamres, and S. N. Bhat, *J. Phys. Chem.*, **75**, 3682 (1971).

7) a) M. Tamres and S. N. Bhat, *J. Am. Chem., Soc.* **94**, 2577 (1972); b) R. A. Singh and S. N. Bhat, *Can. J. Chem.*, **59**, 1212 (1981); c) Ph. D. Thesis of R. A. Singh.

8) P. D. Chattaway and G. Hoyle, *J. Chem. Soc.*, **123**, 654 (1923).

9) W. K. Plucknett and H. L. Richards, *J. Chem. Eng. Data*, **8**, 239 (1963).

10) R. M. Keefer and L. J. Andrews, *J. Am. Chem. Soc.*, **77**, 2164 (1955).

11) H. A. Benesi and J. H. Hildebrand, *J. Am. Chem. Soc.*, **71**, 2703 (1949).

12) a) E. H. Lane, S. D. Christian, and J. D. Childs, *J. Am. Chem. Soc.*, **96**, 38 (1974); b) S. D. Christian, J. D. Childs, and E. H. Lane and D. R. Hershbach, *ibid.*, **94**, 6861 (1972).

13) P. J. Trotter and M. W. Hanna, *J. Am. Chem. Soc.*, **88**, 3724 (1966).

14) L. E. Orgel and R. S. Mulliken, *J. Am. Chem. Soc.*, **79**, 4839 (1957).

15) K. L. Saenger, C. M. McClelland, and D. R. Hershbach, *J. Phys. Chem.*, **85**, 3333 (1981).

16) E. M. Voigt, *J. Phys. Chem.*, **72**, 3300 (1968).

17) M. Murakami, *Bull. Chem. Soc. Jpn.*, **26**, 441 (1953).

18) H. C. Tse and M. Tamres, *J. Phys. Chem.*, **81**, 1376 (1977).